

2604

72 P.

5101-296  
Flat-Plate  
Solar Array Project

DOE/JPL-1012-123  
Distribution Category UC-63b

# Silicon Production in a Fluidized Bed Reactor: Final Report

Naresh K. Rohatgi

(JPL-Publ-86-17) SILICON PRODUCTION IN A  
FLUIDIZED BED REACTOR Final Report (Jet  
Propulsion Lab.) 72 p HC A05/MF A01

N86-25043

CSCL 10A

G3/44 Unclass  
43377

April 1986

Prepared for  
U.S. Department of Energy  
Through an Agreement with  
National Aeronautics and Space Administration  
by  
Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, California

JPL Publication 86-17



TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No. 86-17		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Silicon Production in a Fluidized Bed Reactor: Final Report				5. Report Date April 1986	
				6. Performing Organization Code	
7. Author(s) Naresh K. Rohatgi				8. Performing Organization Report No.	
9. Performing Organization Name and Address JET PROPULSION LABORATORY California Institute of Technology 4800 Oak Grove Drive Pasadena, California 91109 J5574450				10. Work Unit No.	
				11. Contract or Grant No. NAS7-918	
				13. Type of Report and Period Covered JPL Publication	
12. Sponsoring Agency Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes Sponsored by the U.S. Department of Energy through Interagency Agreement DE-AI01-85CE89008 with NASA; also identified as DOE/JPL-1012-123 and as JPL Project No. 5101-296 (RTOP or Customer Code 776-52-61).					
16. Abstract  @ABS Part of the development effort of the JPL in-house technology involved in the Flat-Plate Solar Array (FSA) Project was the investigation of a low-cost process to produce semiconductor-grade silicon for terrestrial photovoltaic cell applications. The process selected was based on pyrolysis of silane in a fluidized-bed reactor (FBR). Following initial investigations involving 1- and 2-in. diameter reactors, a 6-in. diameter, engineering-scale FBR was constructed to establish reactor performance, mechanism of silicon deposition, product morphology, and product purity. The overall mass balance for all experiments indicates that more than 90% of the total silicon fed into the reactor is deposited on silicon seed particles and the remaining 10% becomes elutriated fines. Silicon production rates were demonstrated of 1.5 kg/h at 30% silane concentration and 3.5 kg/h at 80% silane concentration. The mechanism of silicon deposition is described by a six-path process: heterogeneous deposition, homogeneous decomposition, coalescence, coagulation, scavenging, and heterogeneous growth on fines. The bulk of the grown silicon layer appears to be made up of small diameter particles. This product morphology lends support to the concept of the scavenging of homogeneously nucleated silicon. eABA Author					
17. Key Words (Selected by Author(s)) Energy Conversion Engineering			18. Distribution Statement Unclassified-unlimited		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 80	
				22. Price	

5101-296  
Flat-Plate  
Solar Array Project

DOE/JPL-1012-123  
Distribution Category UC-63b

# Silicon Production in a Fluidized Bed Reactor: Final Report

Naresh K. Rohatgi

April 1986

Prepared for  
**U.S. Department of Energy**  
Through an Agreement with  
**National Aeronautics and Space Administration**  
by  
**Jet Propulsion Laboratory**  
California Institute of Technology  
Pasadena, California

JPL Publication 86-17



Prepared by the Jet Propulsion Laboratory, California Institute of Technology,  
for the U.S. Department of Energy through an agreement with the National  
Aeronautics and Space Administration.

The JPL Flat-Plate Solar Array Project is sponsored by the U.S. Department of  
Energy and is part of the National Photovoltaics Program to initiate a major  
effort toward the development of cost-competitive solar arrays.

This report was prepared as an account of work sponsored by an agency of the  
United States Government. Neither the United States Government nor any  
agency thereof, nor any of their employees, makes any warranty, express or  
implied, or assumes any legal liability or responsibility for the accuracy, com-  
pleteness, or usefulness of any information, apparatus, product, or process  
disclosed, or represents that its use would not infringe privately owned rights.

Reference herein to any specific commercial product, process, or service by trade  
name, trademark, manufacturer, or otherwise, does not necessarily constitute or  
imply its endorsement, recommendation, or favoring by the United States  
Government or any agency thereof. The views and opinions of authors expressed  
herein do not necessarily state or reflect those of the United States Government  
or any agency thereof.

This document reports on work done under NASA Task RE-152, Amendment  
419, DOE/NASA IAA No. DE-AI01-85CE89008.

## ABSTRACT

Part of the development effort of the JPL in-house technology involved in the Flat-Plate Solar Array (FSA) Project was the investigation of a low-cost process to produce semiconductor-grade silicon for terrestrial photovoltaic cell applications. The process selected was based on pyrolysis of silane in a fluidized-bed reactor (FBR). Following initial investigations involving 1- and 2-in. diameter reactors, a 6-in. diameter, engineering-scale FBR was constructed to establish reactor performance, mechanism of silicon deposition, product morphology, and product purity. The overall mass balance for all experiments indicates that more than 90% of the total silicon fed into the reactor is deposited on silicon seed particles and the remaining 10% becomes elutriated fines. Silicon production rates were demonstrated of 1.5 kg/h at 30% silane concentration and 3.5 kg/h at 80% silane concentration. The mechanism of silicon deposition is described by a six-path process: heterogeneous deposition, homogeneous decomposition, coalescence, coagulation, scavenging, and heterogeneous growth on fines. The bulk of the grown silicon layer appears to be made up of small diameter particles. This product morphology lends support to the concept of the scavenging of homogeneously nucleated silicon.

Excellent purity of the silicon product was obtained from an FBR equipped with a quartz liner. The product silicon had metallic contaminants less than the detection limits of spark source mass spectroscopy (e.g.,  $\text{Fe} \leq 0.6$  ppma,  $\text{Cr} < 0.02$  ppma,  $\text{Zn} < 0.04$  ppma,  $\text{Co} \leq 0.1$  ppma). Solar cells fabricated from this pure silicon product showed encouraging results and the data are described in this report.



## FOREWORD

The Flat-Plate Solar Array (FSA) Project, initiated in 1975 to develop the technology for low-cost terrestrial photovoltaic arrays, has been managed by the Jet Propulsion Laboratory (JPL) and funded by the Energy Research and Development Agency (ERDA) and by its successor, the U.S. Department of Energy (DOE). To meet the Project's market price goal of \$0.50/peak watt (1975 dollars) of produced electrical energy, the Silicon Material Task was assigned a responsibility of developing a process to produce silicon at a 1986 market price of less than \$14/kg in 1980 dollars.

As one of several parallel technology development efforts, the Project selected for development a high-throughput, two-step process for the production of silicon from silane. A preliminary economic analysis of the output of a 1000-MT/yr silicon production plant involving this two-step silane process indicated an achievable projected price of \$9.50/kg in 1980 dollars.

The first step in the two-step silane process, involves the transformation of metallurgical grade silicon into extremely pure silane. This process was developed by the Union Carbide Corporation (UCC) under a JPL/DOE contract. The process involving this step now is in commercial production.

The second step, involving the conversion of silane into pure silicon, takes place in a fluidized-bed reactor (FBR). This process involves pyrolytic decomposition of silane followed by deposition of the silicon formed onto a fluidized bed of pure silicon seed particles at 650°C.

Both UCC and JPL worked to develop this second step involving the conversion of silane to pure silicon. The objective of the UCC work was to develop a description of the operating requirements and characteristics for long-duration, steady-state operations, while JPL was involved in investigating a fundamental understanding of the process.

Major accomplishments of the JPL in-house experimental work on the fluidized-bed process, which was initiated in early 1976, are summarized as follows:

- (1) The pyrolysis of silane was demonstrated successfully in 1-in., 2-in., and 6-in. diameter FBRs. Reactor performance was characterized with respect to various operating parameters. It was demonstrated successfully that up to 100% concentration of silane in hydrogen can be used in an FBR. Such concentrations are necessary for silicon production at a high throughput.
- (2) Mechanisms were established that described silane pyrolysis and silicon deposition in FBRs.
- (3) Important processing steps, including silicon-seed particle generation, silicon-seed particle cleaning, and FBR operation with a quartz liner, were developed to produce pure silicon product.

PRECEDING PAGE BLANK NOT FILMED

PAGE IV INTENTIONALLY BLANK

The feasibility of the silane-to-silicon conversion in an FBR clearly has been demonstrated on an experimental scale. The technology now is available to industry for carrying out tests on a pilot-plant scale prior to its commercialization.

## ACKNOWLEDGMENT

The author especially thanks Dr. George C. Hsu for his scientific and engineering guidance. The author also thanks Jim Lloyd, Don Feller, and George Malczewski for their valuable laboratory assistance.



## CONTENTS

I.	INTRODUCTION . . . . .	1
A.	DEVELOPMENT OF A SILICON PRODUCTION PROCESS . . . . .	1
B.	GOALS FOR THE JPL IN-HOUSE FBR PROCESS DEVELOPMENT PROGRAM . . . . .	3
C.	PREVIOUS WORK REPORTED ON THE FBR PROCESS CONDUCTED AT JPL . . . . .	3
D.	OBJECTIVES OF REPORT . . . . .	4
II.	EQUIPMENTS AND OPERATING PROCEDURES . . . . .	7
A.	FLUIDIZED-BED REACTOR SYSTEM . . . . .	7
1.	Basic Design . . . . .	7
2.	Silicon Purity Considerations Toward Reactor Design . . . . .	16
3.	Quartz Liner . . . . .	17
B.	SILICON-SEED GENERATION DEVICE . . . . .	20
C.	SILICON CLEANING DEVICE . . . . .	20
III.	EXPERIMENTAL . . . . .	25
A.	RAW MATERIALS . . . . .	25
B.	FLUIDIZED-BED REACTOR EXPERIMENTS . . . . .	25
IV.	EVALUATION OF VARIOUS ANALYTICAL TECHNIQUES . . . . .	29
V.	RESULTS AND DISCUSSIONS . . . . .	31
A.	PERFORMANCE OF SILICON-SEED GENERATION DEVICE . . . . .	31
B.	PERFORMANCE OF THE SILICON CLEANING DEVICE . . . . .	31
C.	PERFORMANCE OF THE SILICON WITHDRAWAL SYSTEM . . . . .	36
D.	FLUIDIZED-BED REACTOR EXPERIMENTS . . . . .	36
1.	Reactor Performance . . . . .	36



2.	Mechanism of Silicon Deposition . . . . .	38
3.	Product Morphology . . . . .	42
4.	Experiments for Further Control of Fines Formation . . . . .	45
5.	Performance of a Quartz Liner . . . . .	45
6.	Product Purity . . . . .	47
7.	Solar Cells . . . . .	49
VI.	CONCLUSIONS . . . . .	57
VII.	RECOMMENDATIONS . . . . .	59
VIII.	REFERENCES . . . . .	61
APPENDIX:	TECHNOLOGY TRANSFER . . . . .	A-1

## Figures

1.	Schematic Diagram for 6-in. Diameter Fluidized-Bed Reactor System . . . . .	9
2.	Engineering Sketch of 6-in. Diameter Fluidized-Bed Reactor . . . . .	11
3.	Six-in. Diameter Fluidized-Bed Reactor . . . . .	12
4.	Gas Distributor for Fluidized-Bed Reactor . . . . .	13
5.	Silicon-Product Withdrawal System . . . . .	14
6.	Overall Silicon-Product Withdrawal and Collection System . .	15
7.	Quartz Liner for the Fluidized-Bed Reactor . . . . .	19
8.	Diagram of Silicon-Seed Particle Generator . . . . .	21
9.	Silicon-Seed Particle Generation Device . . . . .	22
10.	Fluidized-Bed Silicon Cleaning Device . . . . .	24
11.	Effect of Carrier Gas Flow Rate on Jet Mill Grinding . . . .	32
12.	Effect of Silicon Feed Rate on Jet Mill Grinding . . . . .	33

13.	Scanning Electron Micrograph of Silicon Seed Particles from Seed Generation Device . . . . .	34
14.	Performance of Silicon-Product Withdrawal System . . . . .	37
15.	Experimental Silicon Production Rate Versus Silane Concentration . . . . .	39
16.	Scanning Electron Micrographs of the Silicon Product from a Fluidized-Bed Reactor . . . . .	40
17.	Reaction Paths for Silane Pyrolysis in a Fluidized-Bed Reactor . . . . .	41
18.	Morphology of Deposited Layer of Silicon and the Elutriated Fines . . . . .	44
19.	Temperature Profile in 6-in. Fluidized-Bed Reactor Fitted with Quartz Liner . . . . .	48
20.	Czochralski Ingot from a Fluidized-Bed Reactor Product, JPL Run 115 . . . . .	52
21.	Czochralski Ingot from a Fluidized-Bed Reactor Product, JPL Run 503 . . . . .	54

## Tables

1.	Various Wall Materials for the Fluidized-Bed Reactor . . . . .	18
2.	Summary of Experiments with the 6-in. Fluidized-Bed Reactor . . . . .	26
3.	Evaluation of Various Techniques for Analysis of Silicon . . . . .	30
4.	Impurities in Acid-Cleaned Silicon Seed . . . . .	35
5.	Scavenging Effect of a Secondary Silane Injection . . . . .	46
6.	Purity of Product from a Fluidized-Bed Reactor not Equipped with a Liner . . . . .	50
7.	Purity of Product from a Fluidized-Bed Reactor Equipped with a Quartz Liner . . . . .	51
8.	Performance of Solar Cells Fabricated from the Silicon Produced in a Fluidized-Bed Reactor not Equipped with a Liner . . . . .	53
9.	Performance of Solar Cells Fabricated from the Silicon Produced in a Fluidized-Bed Reactor Equipped with a Quartz Liner . . . . .	55

## SECTION I

### INTRODUCTION

The Flat-Plate Solar Array (FSA) Project was initiated in 1975 to develop the technology for the production of low-cost terrestrial photovoltaic arrays. FSA has been managed by the Jet Propulsion Laboratory (JPL) and funded by the Energy Research and Development Agency (ERDA) and by its successor, the U.S. Department of Energy (DOE). The Project was divided up into several tasks dealing with diverse technical fields. Each task was assigned a price goal such that the Project's market-price goal of \$.50/peak watt (1975 dollars) of produced electrical energy could be achieved. The responsibility of the Silicon Material Task was to demonstrate a capability of producing silicon of a purity suitable for the manufacture of terrestrial solar arrays that met the Project's performance requirements for energy conversion. In addition, the silicon produced had to have a 1986 market price of less than \$14/kg (in 1980 dollars) (References 1,2).

In a conventional silicon-producing technology (Siemens process), the hydrogen reduction of trichlorosilane deposits silicon heterogeneously (gas-solid phase) on a hot filament at a very slow rate. A coherent and dense silicon rod is obtained as the product in a batch mode. Homogeneous (gas phase) decomposition is suppressed by limiting the trichlorosilane feed to a low concentration (i.e., <5%). The silicon produced from this process is of semiconductor purity and can be used for solar cell fabrication. The price of silicon produced by this process, however, is of the order of \$60 to \$100/kg, which is much higher than the projected Project goal to produce silicon at less than \$14/kg.

For this reason, the Project funded various low-cost silicon-production processes for preliminary experimental evaluation (References 3,4). A high-throughput silicon-production process that involves fluidized-bed silane pyrolysis was selected for development, both at the Union Carbide Corporation (UCC) and JPL.

#### A. DEVELOPMENT OF A SILICON PRODUCTION PROCESS

A two-step process involving the pyrolysis of silane was developed (References 5,6).

In the first step, metallurgical-grade silicon is transformed into extremely pure silane ( $\text{SiH}_4$ ). This transformation involves six separate operations:

- (1) The production of trichlorosilane ( $\text{SiHCl}_3$ ) from the hydrochlorination reaction of  $\text{H}_2$  and  $\text{SiCl}_4$  with MgSi in a fluidized-bed reactor (References 7,8);



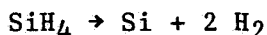
- (2) The purification of the  $\text{SiHCl}_3$  produced by the removal of both high-volatility gases and metals as chlorides. Residual  $\text{SiCl}_4$  is removed by distillation;
- (3) The disproportionation reaction of  $\text{SiHCl}_3$  into dichlorosilane ( $\text{SiH}_2\text{Cl}_2$ ) and  $\text{SiCl}_4$ ;  

$$2 \text{SiHCl}_3 \rightarrow \text{SiH}_2\text{Cl}_2 + \text{SiCl}_4 \text{ (70}^\circ\text{C)}$$
- (4) The purification of the dichlorosilane;
- (5) The disproportionation reaction of dichlorosilane into silane ( $\text{SiH}_4$ ) and trichlorosilane;  

$$3 \text{SiH}_2\text{Cl}_2 \rightarrow \text{SiH}_4 + 2 \text{SiHCl}_3 \text{ (70}^\circ\text{C)}$$
- (6) The purification of the  $\text{SiH}_4$  produced by distillation.

UCC has demonstrated the feasibility of this first step by operating a 100 MT/year silane pilot plant. This reaction now is a commercial process.

In the second step, silane is pyrolytically decomposed to produce pure silicon:



The approach selected for investigation was the thermal decomposition of silane in an FBR. In this process, the silicon released from the silane is deposited on the surface of pure silicon seed particles. The seed particles grow in size at a temperature of  $650^\circ\text{C}$ . The FBR process has the following several advantages:

- (1) It can allow both continuous withdrawal of large silicon particles from the reactor while also permitting the addition of seed particles to the reactor.
- (2) It can be operated at a high-throughput because the large surface area of the silicon seed particles can take advantage of the use of high silane concentrations (e.g.  $>50\%$ ).
- (3) Preliminary calculations indicated the power consumption of less than 20 kWh/kg of silicon produced.
- (4) An economic analysis of a 1000-metric tons/yr silicon-production plant, involving both steps, indicated a price of \$9.50/kg in 1980 dollars (Private communication, Union Carbide Corporation, Washougal, Washington).

A research program was conducted both at UCC and JPL to develop an FBR process. The objective of the UCC work was to develop the process empirically and to demonstrate long-duration operations. JPL, however, was involved in the attainment of fundamental understanding of the process.

## B. GOALS FOR THE JPL IN-HOUSE FBR PROCESS DEVELOPMENT PROGRAM

The JPL in-house goals were:

- (1) To gather experimental data for operating-window and deposition kinetics.
- (2) To develop FBR technology as a means to prepare low-cost photovoltaic material.
- (3) Based on experimental findings, to establish a fundamental understanding of fluidized-bed silicon deposition in terms of homogeneous nucleation and chemical vapor deposition.

## C. PREVIOUS WORK REPORTED ON THE FBR PROCESS CONDUCTED AT JPL

Initial FBR-process development work at JPL was conducted using a 1-in. diameter quartz reactor. Silane concentrations of less than 4% in hydrogen were used to study both the feasibility of silane pyrolysis in an FBR and the morphology of the silicon product. A fluidized-bed particle-growth model was developed based on mass transfer and the controlled steps of both homogeneous and heterogeneous chemical reactions (References 9,10). Further experimental work was conducted in 2-in. and 6-in. diameter FBRs to investigate various FBR subsystems and also to establish FBR operating-windows (References 11,12,13). The important experimental findings are:

- (1) The fluidized bed of silicon particles can be adequately heated by an external resistant heater. Silicon deposition on the reactor wall is not a problem if the reactor is operated according to a proper bed-temperature profile (Reference 13).
- (2) Gas distributors made of porous carbon, multilayer screen, and single-layer 325-mesh screen were all found to be satisfactory for the fluidized-bed operation.
- (3) A water-cooled, copper, cooling coil, located beneath the distributor screen-support plate, was found to be the most effective system to keep the distributor temperature below 300°C. The FBR was operated for 8 h at a 30% silane concentration without any sign of plugging the distributor screen.
- (4) The continuous withdrawal of product particles was successfully demonstrated with a withdrawal rate of 3 kg/h for 8 hours.
- (5) A  $U/U_{mf}$  ratio<sup>1</sup> of 3 to 5 was established as an ideal fluidization condition to carry out the silane pyrolysis reaction without formation of excessive fines (<10%). When the  $U/U_{mf}$  ratio is greater than 5, excessive silicon fines (>10%) are formed.

---

<sup>1</sup>Where  $U$  is the superficial gas velocity and  $U_{mf}$  is the minimum fluidization velocity.

- (6) The efficiency of the conversion of silane to silicon in the FBR is almost 100% at a 650°C bed temperature and a  $U/U_{mf}$  ratio of 5.
- (7) A bed temperature of 630 to 670°C was established as an ideal condition to carry out the silane pyrolysis reaction without formation of excessive silicon fines (<10%).
- (8) Up to 100% silane can be fed into the FBR with fines formation of less than 10%.
- (9) The results, at a bed temperature of 650°C and a  $U/U_{mf}$  ratio of 5, showed that more than 90% of the silicon feed as silane was retained in the bed as deposited material and less than 10% was collected in the filter as elutriated fines. With an increase in silane feed-concentration from 20 to 80%, the rate of silicon product formation increases from 0.9 to 3.5 kg/h. Five FBRs, each of 15 cm diameter, to produce 100 MT/yr of silicon, at a production rate of 3.5 kg/h (reactor) and a 70% on-stream time-factor, are needed. In comparison, a commercial Siemens process, in which silicon is produced strictly by heterogeneous decomposition of trichlorosilane on a heated rod uses a Siemens bell-jar reactor 50 cm diameter x 1.2 m high. Its typical product rate is 0.5 kg/h. To produce 100 MT/yr of silicon by this Siemens technique, 33 bell-jar reactors would be needed compared to only five 15-cm FBRs.
- (10) Based on experimental data, a model was developed to predict rate of silicon particle growth. The rate of growth is a first-order reaction with respect to the concentration of silane in the hydrogen in the feed. The rate constant of the overall particle diameter growth was 13  $\mu\text{m}/\text{h}$  for the given experimental conditions.

#### D. OBJECTIVES OF REPORT

Since the operating-window and silicon-deposition kinetics are well established, research was continued to establish silicon deposition mechanisms and silicon product purity. This report, representing the latest experimental work, discusses the following activities:

- (1) Performance of JPL-developed silicon-seed generation device.
- (2) Performance of JPL-developed silicon-seed cleaning device.
- (3) Performance of an FBR with a quartz liner required to produce a high-purity silicon product.
- (4) Latest experimental work on fluidized-bed silane pyrolysis.
- (5) Mechanism of silicon deposition.

- (6) Data on silicon product morphology.
- (7) Data on silicon product purity.
- (8) Fabrication and characterization of solar cells from the fluidized-bed silicon product.





## SECTION II

### EQUIPMENTS AND OPERATING PROCEDURES

#### A. FLUIDIZED-BED REACTOR SYSTEM

##### 1. Basic Design

The 6-in. FBR system is depicted in Figure 1. The detailed description of an FBR system is discussed in detail elsewhere (Reference 13). The FBR consists of a reactor constructed from 6-in., schedule 40 stainless steel 316 pipe, and has dimensions of 6.065 in. inside diameter (I.D.) x 48 in. high. The reactor has an expanded head of 24 X 24 in. to allow entrained particles to drop back into the bed (Figures 2 and 3). Particles in the bed are fluidized by a gas distributor fabricated from one layer of a 325 mesh stainless steel screen supported by a 1/20-in.-thick plate with 1/8-in.-diameter multiple holes. The gas distributor is water cooled to keep its temperature below 350°C. There is water cooling at the periphery of the distributor in addition to a water-cooled copper cooling coil located beneath the gas distributor. The copper cooling coil was silver soldered to a 1/20-in.-thick plate with multiple holes. The distributor screen is spot welded to the support plate to ensure firm contact (Figure 4).

To maintain a constant bed height in the reactor, the 6-in. diameter FBR also is equipped with a continuous silicon withdrawal system (Figures 5 and 6). It is designed to withdraw silicon particles at a rate up to 3 kg/h. It consists of an externally water-cooled, silicon withdrawal tube, 15 in. long x 0.87 in. I.D. The particles in the silicon withdrawal tube were fluidized at a  $U/U_{mf}$  ratio of one to:

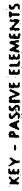
- (1) Keep silane out of the withdrawal tube.
- (2) Permit accumulation of large particles in the tube.
- (3) Minimize the disturbance caused by the gas velocity on the fluidization characteristics in the bed.
- (4) Cool the tube more effectively by preventing a sudden fall downward of hot bed particles.

Located at the bottom of the withdrawal tube is an electronically controlled pinch valve. This valve is opened for a duration of 1s to allow particles to drop into a tee. The opening of the valve is carried out at a predetermined frequency at 10 to 15 s intervals to allow cooling of the hot silicon particles in the tube. The particles in the tee are transported pneumatically to a cyclone separator and collected in a silicon holding tank of 10 kg capacity (Figure 6).

The reactor was externally heated by a two-zone, fast-response, 12-in.-high, silicon carbide heater with a total output of 9 kw. Both zones are independently controlled to achieve an isothermal condition in the bed within 3 in. from the distributor. Atop the silicon carbide heater is a



**FOLDOUT FRAME**



1. HYGROMETER	10. FACILITY NITROGEN BANK
2. EXHAUST FILTER	11. VACUUM PUMP
3. SAMPLE FILTER	12. GAS CHROMATOGRAPH
4. DIFFERENTIAL PRESSURE GAUGE	13. RELIEF VALVE
5. TOTAL PRESSURE GAUGE	14. NITROGEN FILTER
6. SOLENOID VALVE	15. REACTOR
7. HYDROGEN BANK	16. SAMPLE TUBE
8. INERT GAS BANK	17. EXHAUST SYSTEM
9. SILANE BANK	18. OIL TRAP

Figure 1. Schematic Diagram for 6-in. Diameter Fluidized-Bed Reactor System



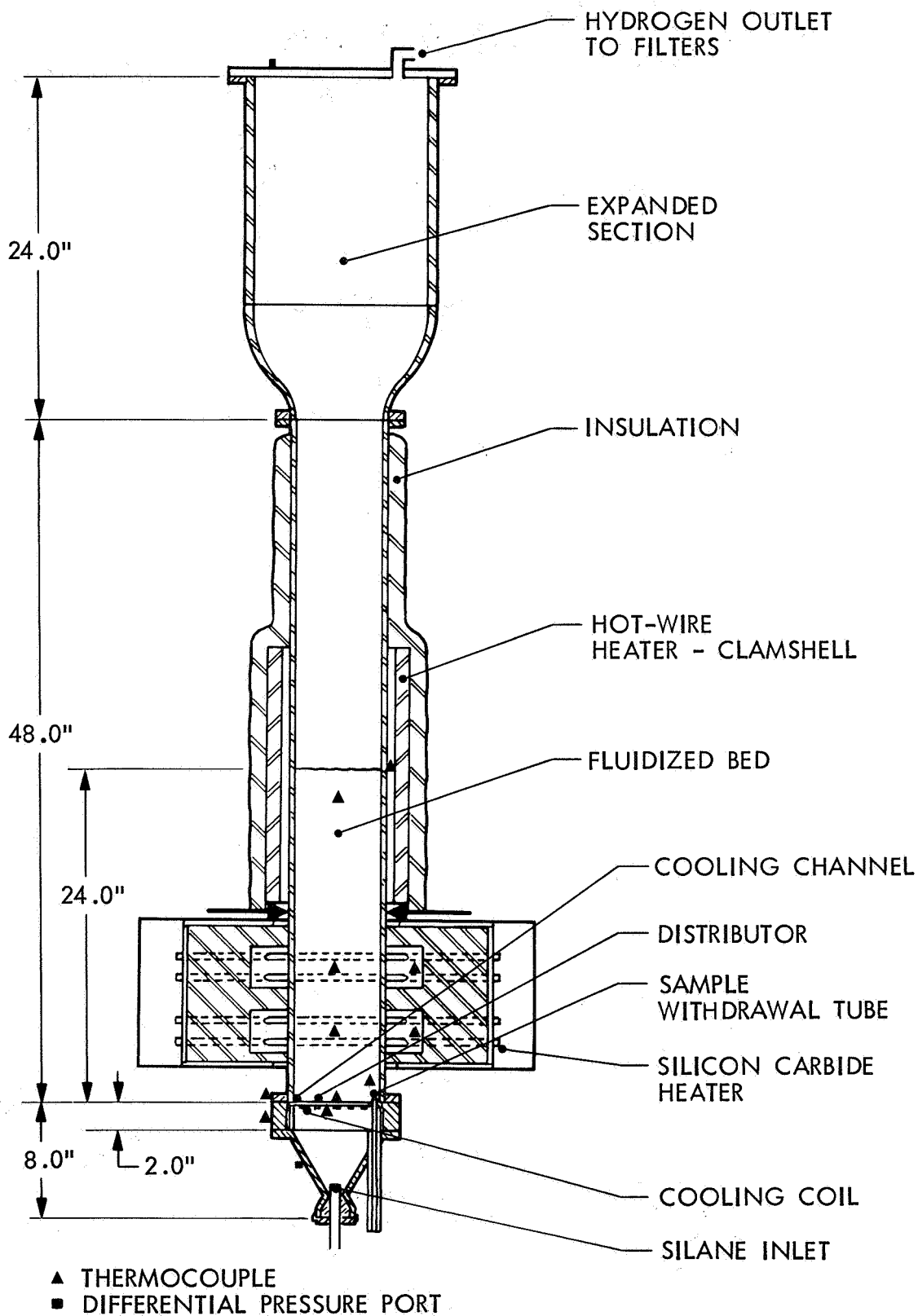


Figure 2. Engineering Sketch of 6-in. Diameter Fluidized-Bed Reactor

ORIGINAL PAGE IS  
OF POOR QUALITY

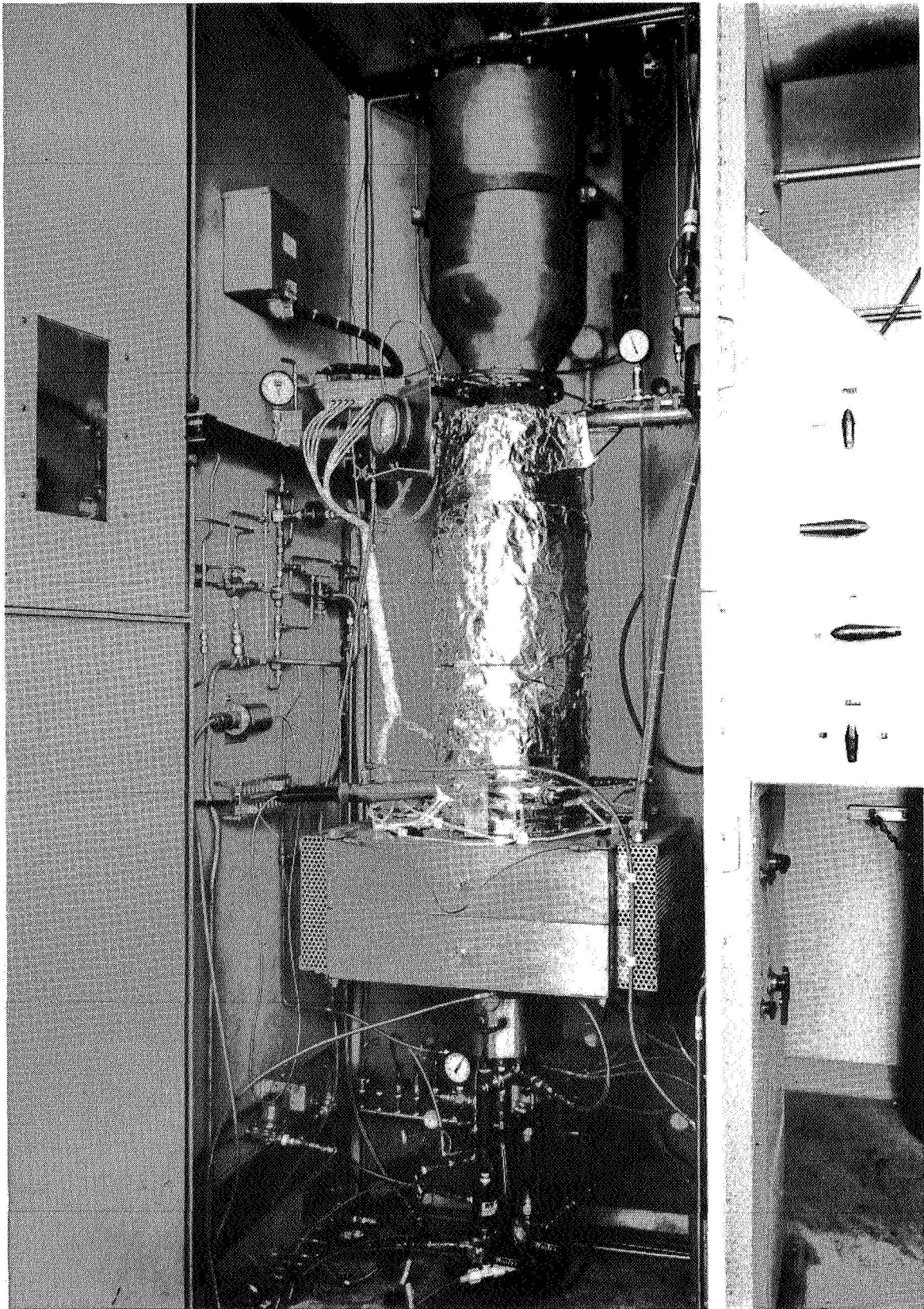


Figure 3. Six-in. Diameter Fluidized-Bed Reactor

ORIGINAL PAGE IS  
OF POOR QUALITY

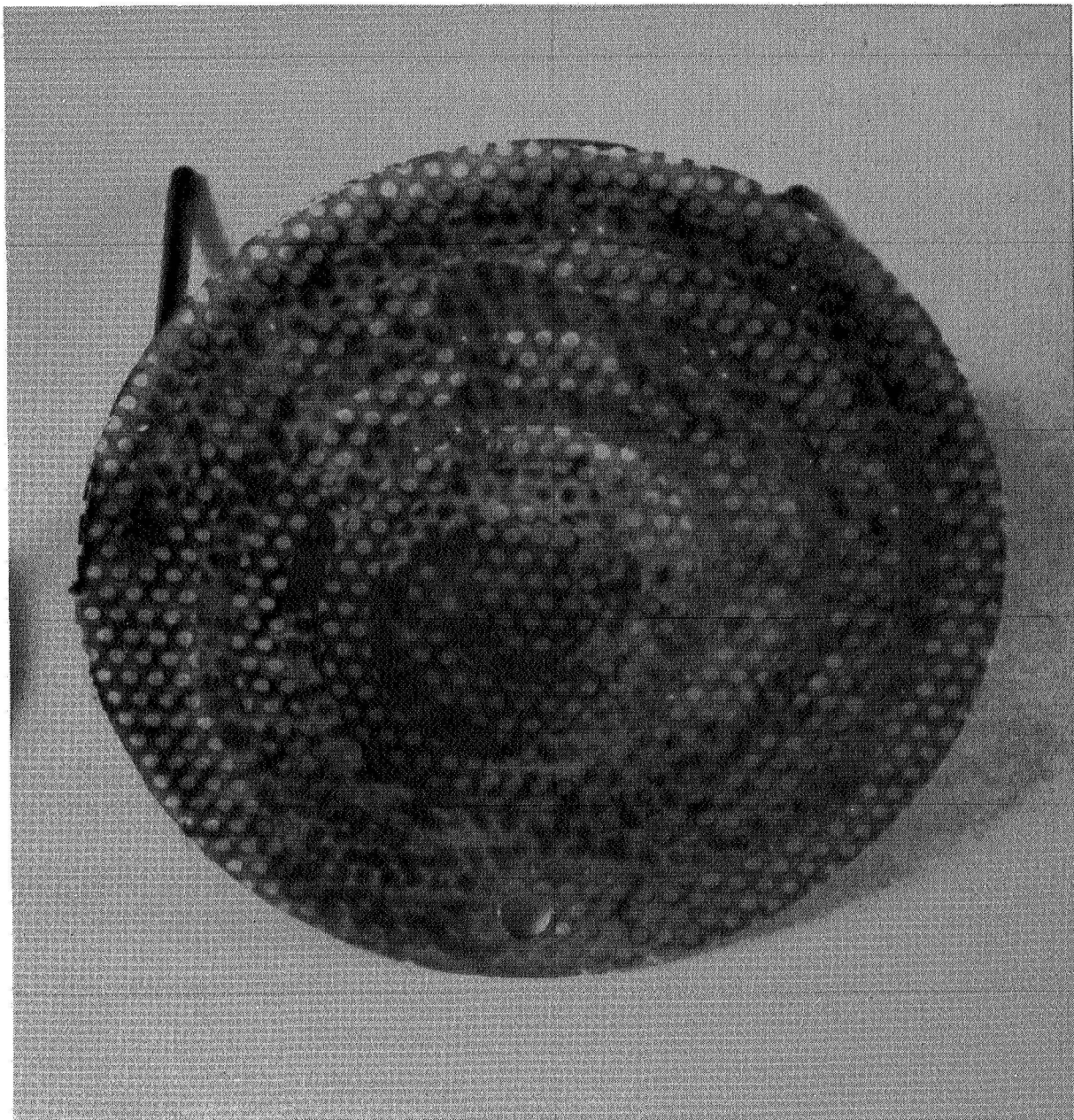


Figure 4. Gas Distributor for Fluidized-Bed Reactor



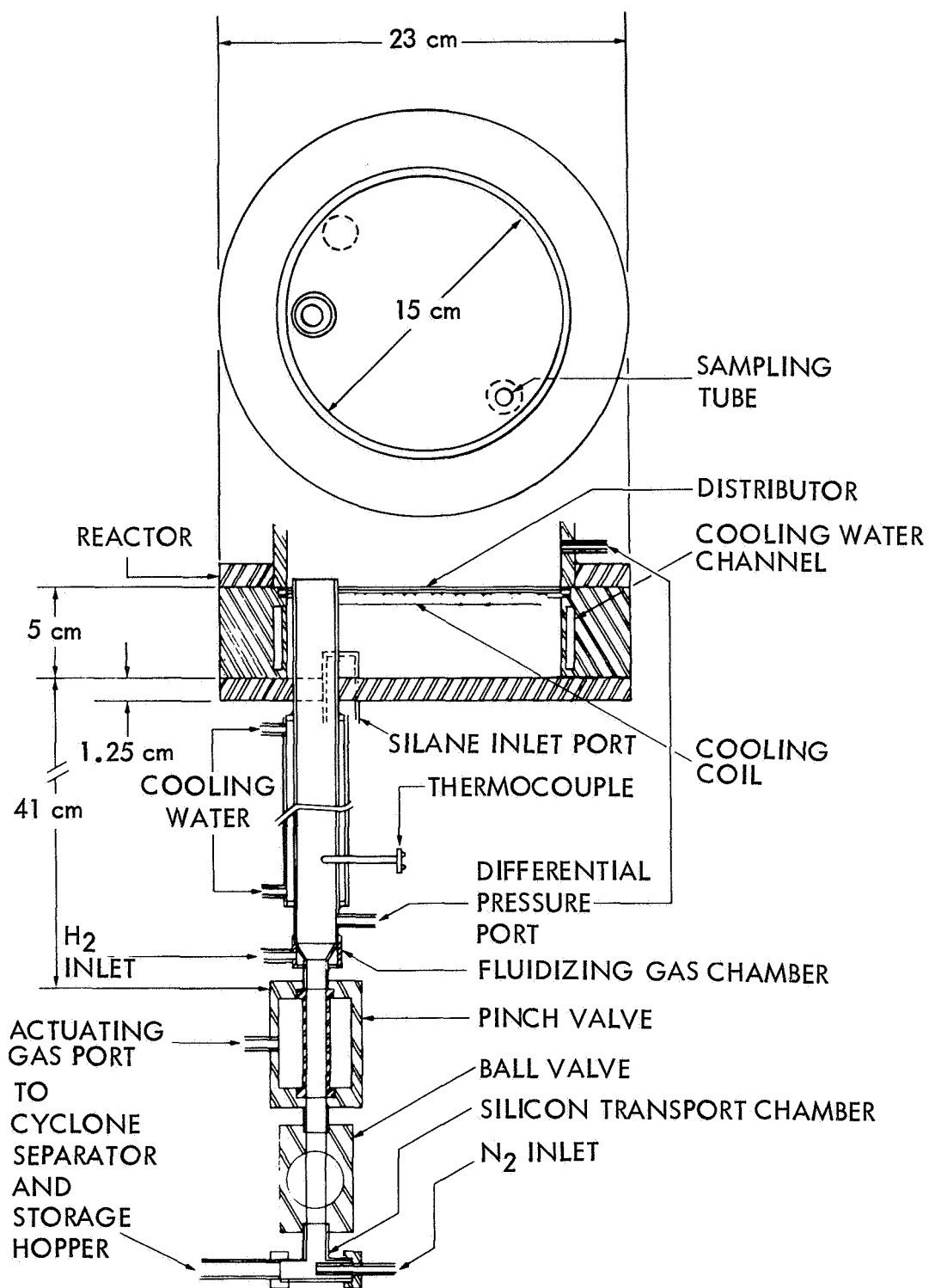


Figure 5. Silicon-Product Withdrawal System



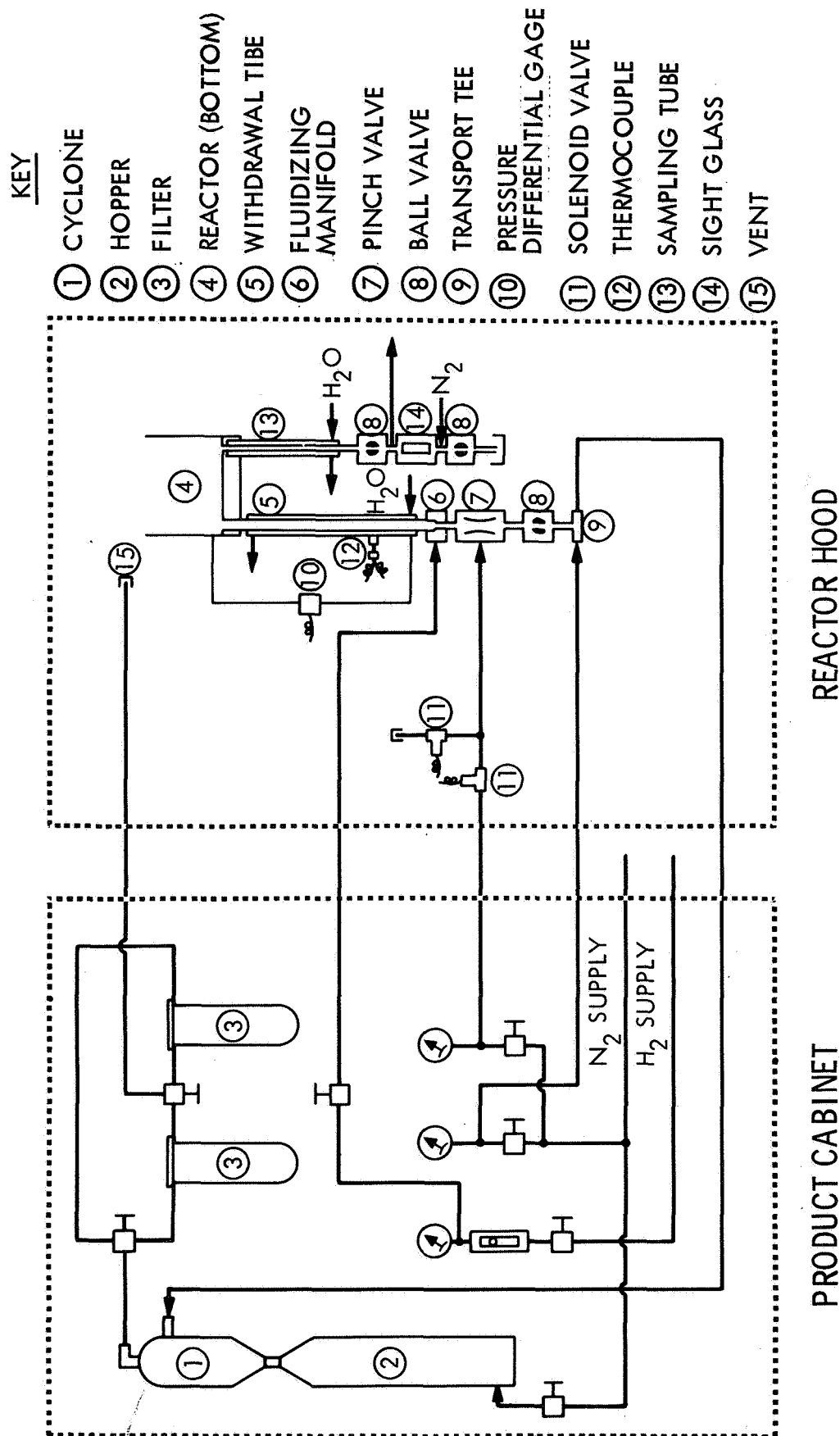


Figure 6. Overall Silicon-Product Withdrawal and Collection System

single-zone, independently controlled, 18-in. high, ceramic clamshell heater with a heating element made of an alloy of iron (72%), chromium (22%), cobalt (0.5%), and aluminum (5.5%). It has a total power output of 9 kw. The main purpose of the clamshell heater is to provide thermal insulation around the reactor and to distribute the heat input throughout the bed height. By helping to keep the temperature difference between the reactor wall and the bed within 50°C, the risk of deposition of silicon on the reactor wall is minimized.

The reactor temperature was continuously monitored by type K iron-constantan thermocouples located at various heights within the bed, on the reactor wall, and on the gas distributor. The temperature was continuously recorded by a Leeds & Northrup recorder. The pressure drop across the gas distributor and the bed as well as the total pressure were monitored. The flow rates of silane and hydrogen were monitored by Brooks rotameters. The compositions of both the inlet and outlet silane-hydrogen gas mixtures were analyzed by a Hewlett-Packard gas chromatograph equipped with a Porapack-Q column.

The two silicon carbide heaters in the 6-in. diameter FBR were independently controlled by silicon-controlled rectifier (SCR) power controllers. The temperature was controlled by an OMEGA Dual Set-point controller. The electrical resistance heater in the 6-in. FBR was regulated by a Thermcraft Controller.

The detailed operating procedure for the FBR system is discussed elsewhere (Rohatgi, N.K., "Six-inch FBR Operating Procedure," JPL Internal Document, 1982). The reactor was charged with clean silicon seed and preheated to the desired bed temperature with a hydrogen gas velocity equivalent to five times the minimum velocity required to fluidize the particles. The silane was gradually fed into the FBR, followed by a gradual decrease in the hydrogen flow rate to obtain the desired silane concentration. The reactor was operated at 5 psig pressure for a planned duration. Experiments were conducted both in a batch mode as well as the continuous-withdrawal mode to maintain a constant bed height in the reactor. The pressure-drop fluctuation across the bed was continuously monitored by a differential pressure transducer. The pressure-fluctuation signal was used to monitor the fluidization behavior of the bed.

The exit gas from the 6-in. FBR was passed through 1  $\mu$ m porosity CUNO filters before being flared off. The purpose of these filters is to determine the extent of silicon fines elutriation. At the end of an experiment, the silicon in the bed was recovered, weighed, and screened to obtain the average particle size of the product. The silicon fines in the filters and the expanded head, including the lines to the filters, were also recovered and weighed to establish complete mass-balance. The percentages of silicon recovered in the bed and as fines were based upon the total silicon input to the reactor.

## 2. Silicon Purity Considerations Toward Reactor Design

Fluidized-bed processing of silicon particles poses a serious problem of reactor wall erosion that can lead to metallic impurity

contamination of the produced silicon. Major reactor components that have been identified as sources of metallic contamination are:

- (1) The 4 ft. tall FBR section.
- (2) The 2 ft. tall expanded head
- (3) The gas distributor
- (4) Silicon-withdrawal assembly

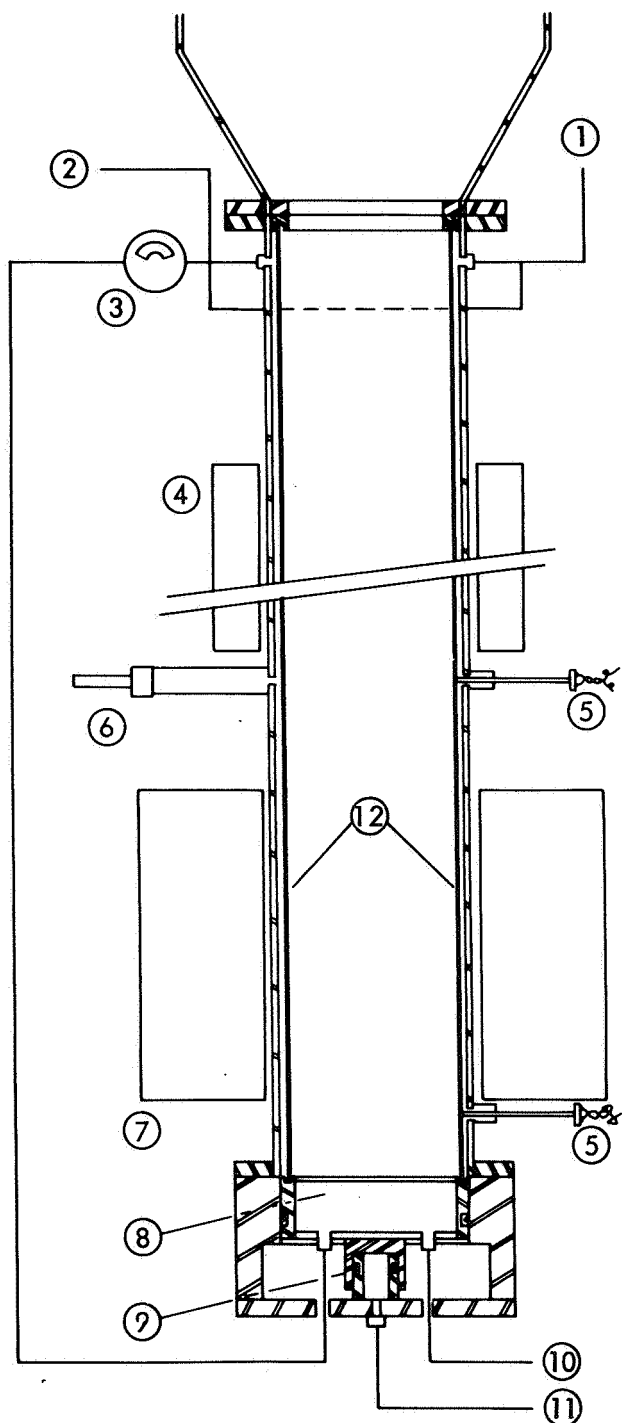
Because the FBR component is exposed to a 650°C temperature it is anticipated that maximum wall erosion will occur in this section. The other reactor components are exposed to temperatures less than 250°C. In these sections, silicon particles are not violently fluidized. With these criteria in mind, the following various materials were considered for walls of the reactor: quartz liner, silicon carbide liner, silicon liner, silicon carbide coated graphite reactor, zirconium oxide protective coating on stainless steel reactor, and liquid nitriding of various stainless steel reactor components (Table 1). Each of these wall materials has certain advantages and disadvantages with respect to heat transfer, mechanical strength, cost, and potential for metallic contamination. After a thorough evaluation, it was decided to liquid nitride the reactor's expanded head, gas distributor, and silicon withdrawal assembly to increase the hardness of exposed stainless steel surfaces. This process involves the treatment of various stainless steel parts in a bath of liquid cyanide. The exposed stainless steel surface of the FBR section is isolated from the silicon particles by insertion of a mechanically sealed quartz liner.

### 3. Quartz Liner

Quartz is an excellent choice for a reactor liner from the point of view of silicon purity. Breakage of the liner during thermal cycling, however, is a serious problem. The deposition of silicon on either the inside or outside surface of quartz will break the liner because of the differential thermal expansion between silicon and quartz. Since the inside surface of the quartz liner is exposed to the hot silicon particles, silicon deposition can be controlled by maintaining a proper temperature gradient between the particles and reactor wall. If silane is permitted to flow in between the quartz liner and the stainless steel wall, the silicon will deposit on the quartz tube and eventually break it during thermal cycling. The design criterion, therefore, was to establish seals for the quartz liner between the expanded head flange and the gas distributor. This would prevent silane from flowing into the annular space between the quartz liner and the stainless steel reactor wall. The quartz liner design, shown in Figure 7, consists of a 5.75-in. outside diameter x 4-ft-long quartz tube with 1/8-in. wall thickness. The top end of the quartz liner is supported against a ring with a 1/4-in. groove and a Graphoil gasket. The bottom end of the quartz liner stands on a piston gas-distributor assembly with 1/4-in. groove and a quartz sleeve used as a gasket. The outside surface of the piston consists of a pneumatic cylinder mounted against the reactor flange. The interface is vacuum and pressure sealed with a viton O-ring. The entire assembly is water cooled to maintain integrity of the O-ring.

Table 1. Various Wall Materials for the Fluidized-Bed Reactor

FBR WALL MATERIALS	DESCRIPTION	ADVANTAGES	DISADVANTAGES	DECISION
QUARTZ LINER IN STAINLESS STEEL REACTOR	PLACED A MECHANICALLY SEALED QUARTZ TUBE INSIDE THE SS REACTOR	<ul style="list-style-type: none"> <li>• AVOIDS METAL CONTAMINATION</li> <li>• INEXPENSIVE CONSTRUCTION</li> </ul>	<ul style="list-style-type: none"> <li>• POOR HEAT TRANSFER</li> <li>• QUARTZ MAY CRACK</li> </ul>	LINER FOR FLUIDIZED-BED REACTOR SECTION
SILICON CARBIDE LINER IN STAINLESS STEEL REACTOR	SAME (WITH SiC TUBE)	<ul style="list-style-type: none"> <li>• AVOIDS METAL CONTAMINATION</li> </ul>	<ul style="list-style-type: none"> <li>• POOR HEAT TRANSFER</li> <li>• POSSIBLE CARBON CONTAMINATION</li> <li>• EXPENSIVE CONSTRUCTION</li> </ul>	X
SILICON LINER IN STAINLESS STEEL REACTOR	SAME (WITH Si TUBE)	<ul style="list-style-type: none"> <li>• AVOIDS METAL CONTAMINATION</li> </ul>	<ul style="list-style-type: none"> <li>• POOR HEAT TRANSFER</li> <li>• RELATIVELY EXPENSIVE CONSTRUCTION</li> </ul>	X
SILICON CARBIDE COATED GRAPHITE REACTOR	INSIDE SURFACE OF GRAPHITE TUBE IS COATED WITH SILICON CARBIDE	<ul style="list-style-type: none"> <li>• GOOD HEAT TRANSFER</li> </ul>	<ul style="list-style-type: none"> <li>• NON-UNIFORM COATING</li> <li>• POSSIBLE CARBON CONTAMINATION</li> <li>• EXPENSIVE CONSTRUCTION</li> </ul>	X
ZIRCONIUM OXIDE COATING ON SS REACTOR	INSIDE SURFACE OF THE SS REACTOR IS COATED WITH ZIRCONIUM OXIDE	<ul style="list-style-type: none"> <li>• GOOD HEAT TRANSFER</li> </ul>	<ul style="list-style-type: none"> <li>• POSSIBLE ZIRCONIUM CONTAMINATION</li> <li>• CRACKING OF COATING DUE TO DIFFERENTIAL THERMAL EXPANSION</li> </ul>	X
LIQUID NITRIDING OF SS	HARDNESS OF SS SURFACE IS INCREASED BY TREATING IT IN A LIQUID CYANIDE BATH	<ul style="list-style-type: none"> <li>• INEXPENSIVE PROCESS</li> </ul>	<ul style="list-style-type: none"> <li>• POSSIBLE MIGRATION OF METALLIC IMPURITIES FROM HOT SS SURFACE</li> </ul>	GAS DISTRIBUTOR, EXPANDED HEAD, AND WITHDRAWAL ASSEMBLY WILL BE TREATED BY THIS PROCESS
X = NOT SELECTED FOR THIS STUDY SS = STAINLESS STEEL				



- ① HYDROGEN EXHAUST
- ② HYDROGEN INLET
- ③ DIFFERENTIAL PRESSURE GAGE
- ④ CLAMSHELL HEATER
- ⑤ THERMOCOUPLE
- ⑥ PYROMETER
- ⑦ SILICON CARBIDE HEATER
- ⑧ PISTON
- ⑨ PNEUMATIC CYLINDER
- ⑩ SILANE INLET
- ⑪ NITROGEN INLET
- ⑫ QUARTZ LINER

Figure 7. Quartz Liner for the Fluidized-Bed Reactor

The quartz-lined reactor, filled with silicon particles, is closed and evacuated to remove oxygen prior to heating. The silicon particles are fluidized with a flow of nitrogen or helium. A pressure of 200 psig is applied at the pneumatic cylinder to mechanically seal the top end of the quartz liner against the Graphoil gasket. The pressure at the pneumatic cylinder compensates, in the axial direction, for the differential thermal expansion between the stainless steel reactor wall and the quartz liner. The bottom end of the quartz liner is not completely sealed and hydrogen is permitted to flow at a rate of less than 1 SLPM. During the entire heating cycle, as well as during the silicon deposition experiment, a differential positive pressure of a 20-in. water column is maintained between the annular space and the inlet port for the silane/hydrogen gas mixture. This procedure ensures that hydrogen can leak into the reactor but that the silane/hydrogen mixture cannot leak into the annular space.

#### B. SILICON-SEED GENERATION DEVICE

A prior technique for preparing fluidized-bed seed involved grinding bulk, semiconductor-grade silicon with a mechanical crusher followed by a leaching treatment with acids. Not only are these efforts tedious and costly, but the grinding tends to introduce metallic contaminants. A jet-milling technique for seed-particle generation, using impinging jets of gas to grind silicon was studied in this work. Specifically, this technique involved the grinding of silicon particles through the impingement of two opposing nitrogen jets that carry silicon particles. The jet-milling device and its dimensions are shown in Figures 8 and 9. The device is lined with polyurethane and high-density polypropylene to avoid exposure of silicon to metallic surfaces. It has an impact chamber 0.75-in. diameter x 2-in. long. The device is equipped with two opposing nitrogen jets, each with an orifice diameter of 0.078 in. Large silicon particles (<2mm) are fed in at the top of the device and are carried into the impact chamber by the two opposing nitrogen jets at a supersonic velocity. Collisions of the large particles result in their fracture into smaller-sized particles. The fractured particles, carried by the effluent gas, are discharged through a 1-in. diameter pipe into a cyclone separator and are collected in a polyethylene jar at the bottom of the separator. The small particles (<50  $\mu\text{m}$ ) in the discharged nitrogen gas stream are collected in an air bag filter. Using screens constructed out of polyethylene and polypropylene, the fractured particles are separated into three categories of sizes: undersize (<111  $\mu\text{m}$ ), desired size (111 to 400  $\mu\text{m}$ ), and oversize (>400  $\mu\text{m}$ ). The undersized particles are discarded while the oversized particles are recycled back into the seed generation device. After screening, the desired-size seed particles require acid cleaning. The use of a fluid-grinding technique, results, however, in particles with a much lower level of metallic impurities.

#### C. SILICON CLEANING DEVICE

The large silicon particles (<2 mm), as well as the silicon-seed particles, of 111 to 400  $\mu\text{m}$  in diameter, are contaminated with metallic impurities in the ppma range. The removal of these impurities is necessary prior to conducting an experiment to grow semiconductor-grade silicon particles. The average diameter of a seed particle is approximately 250  $\mu\text{m}$

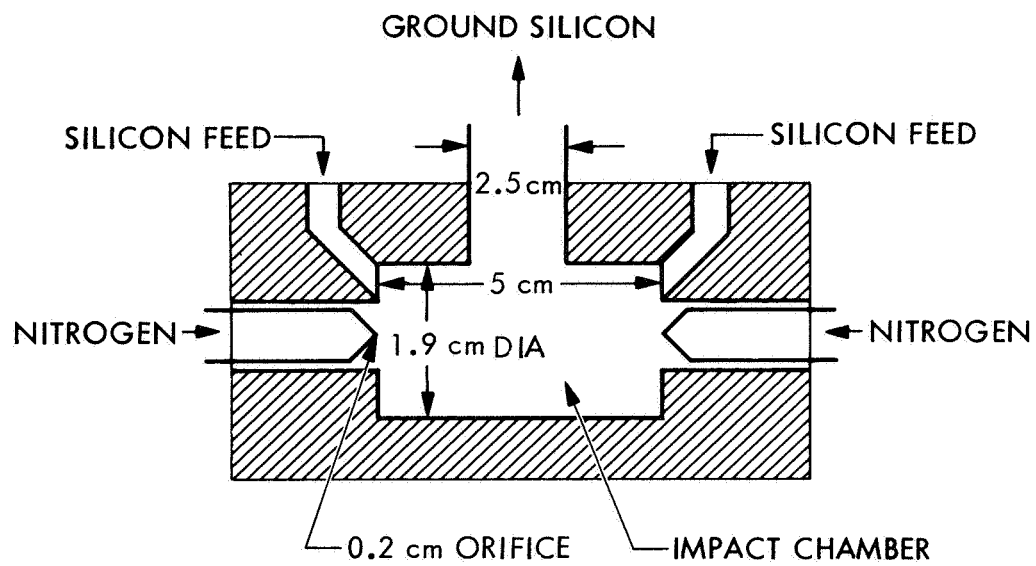


Figure 8. Diagram of Silicon-Seed Particle Generator

ORIGINAL PAGE IS  
OF POOR QUALITY

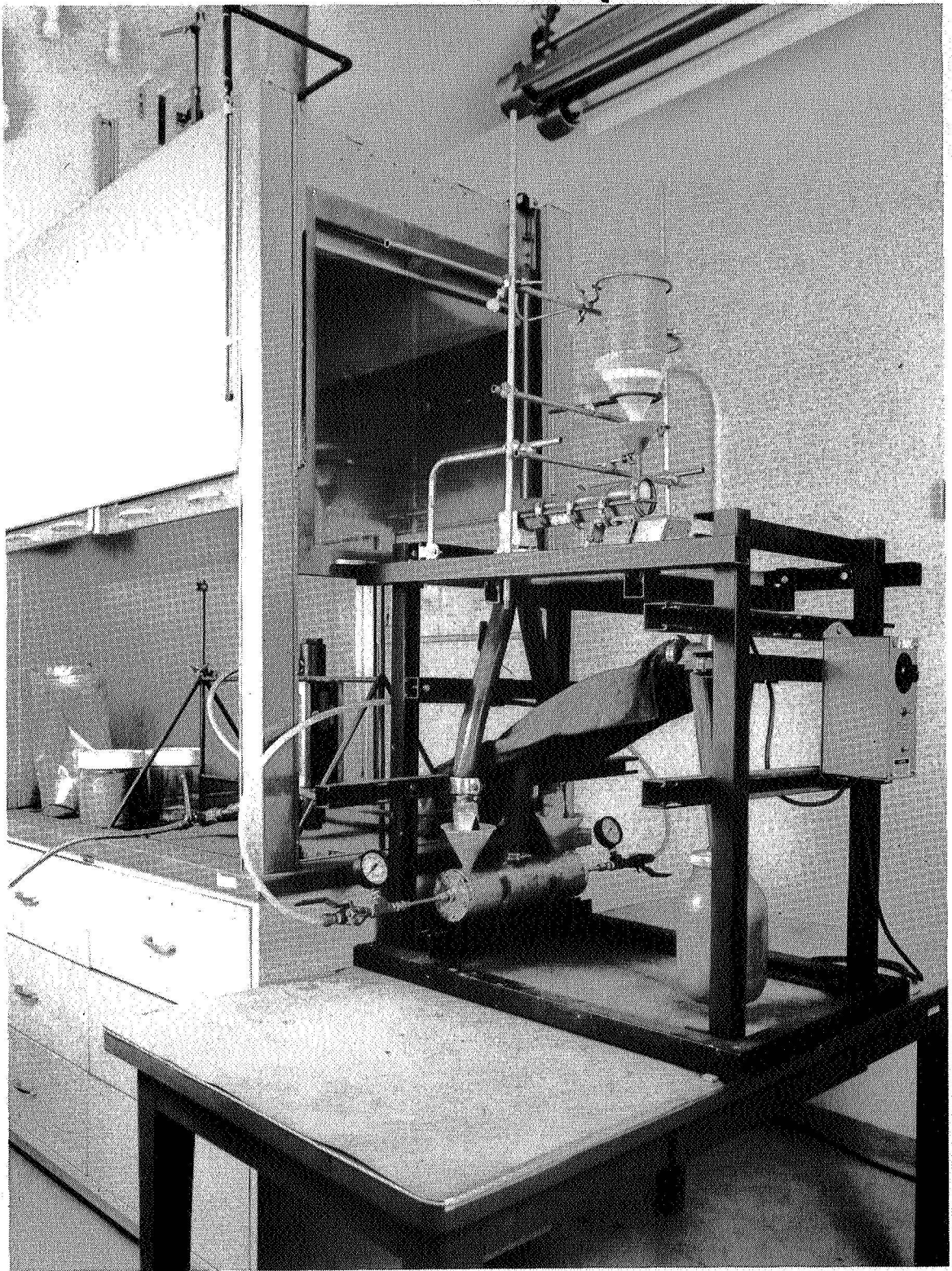


Figure 9. Silicon-Seed Particle Generation Device



and it has a huge surface area per unit weight of the bed. Acid leaching is used to remove metallic impurities from individual silicon particles. Because the cleaning acid is a mixture of concentrated nitric and hydrochloric acids that reacts very fast with metallic impurities to form soluble complexes, it is logical to assume that the silicon cleaning process is mass-transfer limited. The most important design criterion for a silicon cleaning device, therefore, is to provide very good mixing.

In the silicon cleaning device, depicted in Figure 10, silicon particles are fluidized by the cleaning solution. The entire system, in contact with either silicon or acid, is constructed out of polyethylene and polypropylene. It consists of three plastic bottles, each 3.5 in. diameter x 8 in. high that can hold up to 500 grams of silicon (4-in. bed height). The bottom of each bottle is equipped with a 50  $\mu$ m-pore diameter plastic screen and distributor to provide a tangential flow of cleaning solution for good mixing. The top of the bottle is equipped with another 75  $\mu$ m-pore diameter screen to retain the particles within the bottles. The three bottles are installed in a plastic tank filled with up to 2 gallons of cleaning solution that is circulated through the system via a plastic pump (Figure 10). The flow rate of the cleaning solution is adjusted by a plastic needle valve to obtain desired fluidization of silicon particles.

The preparation of cleaned silicon seed by this device includes the following steps:

- (1) A wash with deionized water, in a fluidized-bed mode, to remove fine silicon particles of less than 75  $\mu$ m in diameter.
- (2) Cleaning with a mixture of two parts of 12N HCl and one part of 16N HNO<sub>3</sub> in a fluidized-bed mode for 20 min.
- (3) Acids are drained after 20 min and the particles are washed with deionized water in a fluidized-bed mode until the effluent water is neutral.
- (4) The silicon particles are etched with 48% hydrofluoric acid (HF) in a fluidized-bed mode for 20 min.
- (5) The HF is drained after 20 min and particles are washed with deionized water in a fluidized-bed mode until the effluent water is neutral and has a resistivity of 16 M $\Omega$ .
- (6) The wet particles are dried in a diffusion furnace at 150°C under a nitrogen gas blanket.
- (7) After drying, particles are transferred into a plastic bag that then is sealed.

The effectiveness of this cleaning technique will be discussed later.

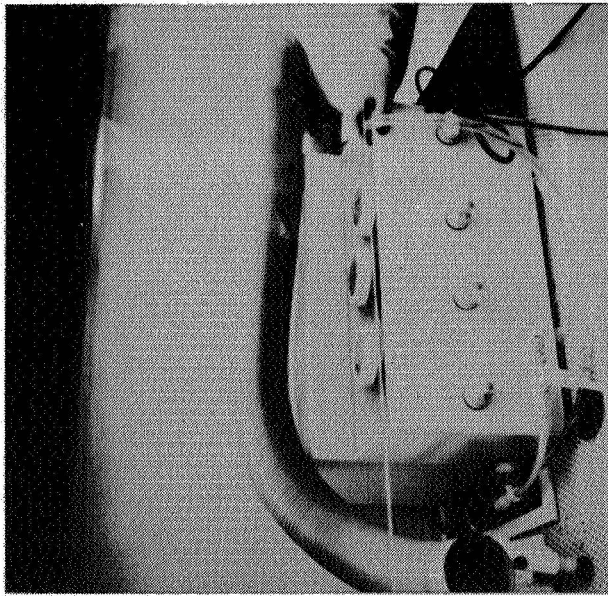
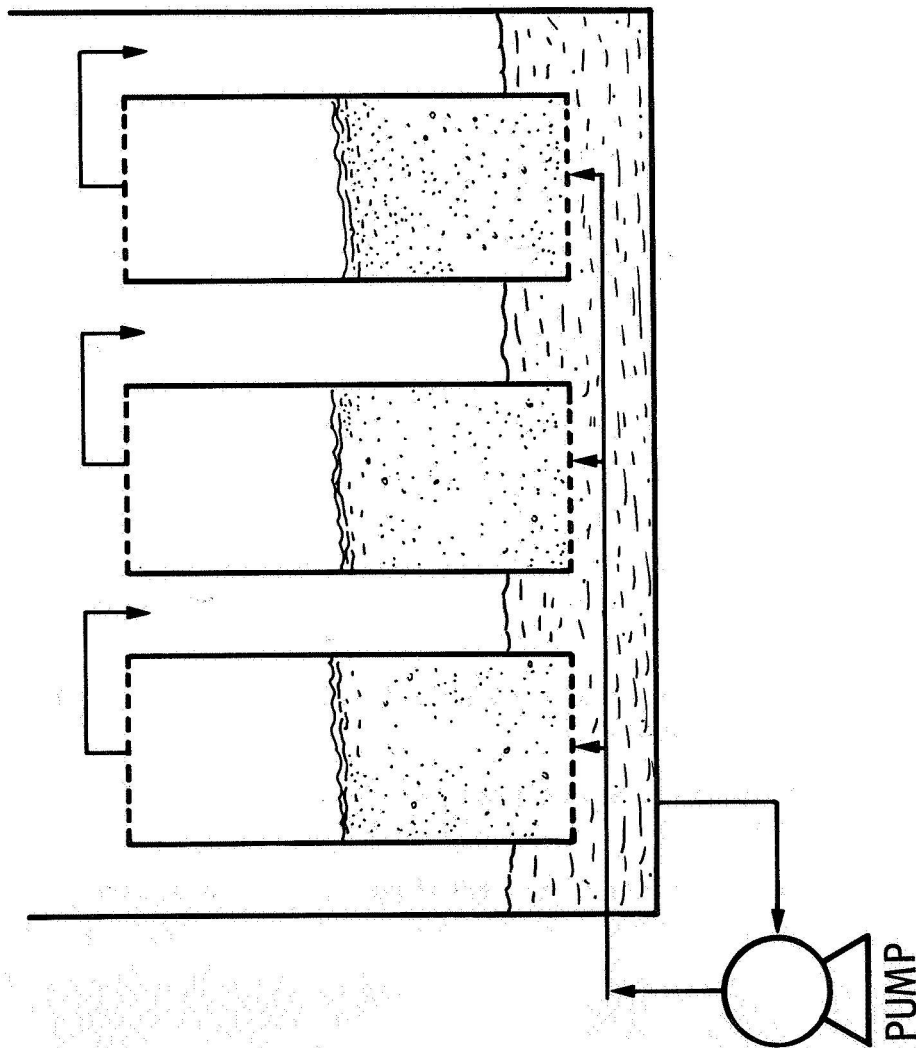


Figure 10. Fluidized-Bed Silicon Cleaning Device

## SECTION III

### EXPERIMENTAL

#### A. RAW MATERIALS

Electronic grade silane was purchased from the Union Carbide Corporation (UCC), Washougal, Washington. The silane-production process was developed as part of the FSA Project. The silicon epitaxial layer obtained by using this silane as a source of silicon has a resistivity of 200 ohms-cm N type. High-purity nitrogen and helium were purchased from Linde, a division of UCC.

Silicon particles of less than 2 mm diameter were purchased from Dynamit Nobel, Italy. These particles were prepared by Dynamit Nobel using a technique that involves the mechanical breaking of a Siemens silicon rod. This silicon has a resistivity greater than 70 ohm-cm N type and greater than 1000 ohm-cm P type.

#### B. FLUIDIZED-BED REACTOR EXPERIMENTS

A summary of all recent FBR experiments is presented in Table 2. The FBR was operated at a bed temperature of 650°C, a  $U/U_{mf}$  ratio of 4 to 5, and silane concentrations ranging from 30 to 50% in hydrogen. Experiments were designed to meet the following objectives:

- (1) Conduct experiments to evaluate reactor performance.
- (2) Conduct experiments to further the control of the formation of fines: Run Numbers 201 to 206.
- (3) Conduct experiments to evaluate performance of a quartz liner: Run. Numbers 300, and 402 to 408.
- (4) Establish purity of the silicon product: Run Numbers 502 and 503.

Table 2. Summary of Experiments with the 6-in. Fluidized-Bed Reactor

RUN NO.	REACTOR LINER	OBJECTIVES	SILICON SEED			EXPERIMENTAL CONDITIONS				PRO- DUCTION RATE (kg/h)	OVERALL MASS- BALANCE		REMARKS
			WEIGHT (kg)	dP ( $\mu$ m)	CLEAN- ING	TEMP (°C)	SILANE CONCEN- TRATION (%)	DURA- TION (h)	U/ U <sub>mf</sub>		% IN BED	% AS FINES	
201	NO	CHECK-OUT FBR SYSTEM	11	247.5	NO	650	30	1	4	X	X	X	INITIAL EXPERIMENT TO CHECK-OUT FBR
202	NO	BLANK FOR FINES CONTROL EXPERIMENT	11	250	NO	650	50	3	4	2.2	87.5	9.25	<ul style="list-style-type: none"><li>PART OF THE BED WAS PLUGGED</li><li>DATA ARE UNRELIABLE</li></ul>
203	NO	FINES CONTROL EXPERIMENT	10.7	250	NO	650	50	3	4	2.15	84	14.9	<ul style="list-style-type: none"><li>PART OF THE BED WAS PLUGGED</li><li>DATA ARE UNRELIABLE</li></ul>
204	NO	FINES CONTROL EXPERIMENT	13	227.2	NO	650	50	3	X	1.5	95.5	6.2	<ul style="list-style-type: none"><li>DATA ARE RELIABLE</li></ul>
206	NO	BLANK FOR FINES CONTROL EXPERIMENT	12.8	223	NO	650	50	3	X	1.3	92	9.4	<ul style="list-style-type: none"><li>DATA ARE RELIABLE</li></ul>
300	QUARTZ	<ul style="list-style-type: none"><li>TEMPERATURE PROFILE</li><li>HEATER PERFORMANCE</li></ul>	11	211	NO	650	0	2	4	0	X	X	<ul style="list-style-type: none"><li>TEMPERATURE PROFILE CAN BE MAINTAINED</li><li>QUARTZ DID NOT CRACK</li></ul>
402	QUARTZ	<ul style="list-style-type: none"><li>TEMPERATURE PROFILE UNDER SILANE FLOW</li></ul>	9	228	NO	650	10	1	4	0.28	X	X	<ul style="list-style-type: none"><li>TEMPERATURE PROFILE CAN BE MAINTAINED</li><li>QUARTZ DID NOT CRACK</li></ul>
406	QUARTZ	LONG DURATION TEST FOR QUARTZ LINER	9	254	NO	650	30	4	5	1.8	90	7.2	<ul style="list-style-type: none"><li>PARTICLES WITHDRAWN AT 2 h INTERVAL</li><li>QUARTZ DID NOT CRACK</li></ul>

Table 2. (Cont'd)

RUN NO.	REACTOR LINER	OBJECTIVES	SILICON SEED			EXPERIMENTAL CONDITIONS				PRO- DUCTION RATE (kg/h)	OVERALL MASS- BALANCE		REMARKS
			WEIGHT (kg)	dP ( $\mu\text{m}$ )	CLEAN- ING	TEMP (°C)	SILANE CONCENTRATION (%)	DURATION (h)	U/ U <sub>mf</sub>		% IN BED	% AS FINES	
407	QUARTZ	TEST FOR HIGH SILANE CONCENTRATION	9	244	NO	650	50	1	4	2.23	89.2	6.1	<ul style="list-style-type: none"> <li>QUARTZ LINER DID NOT CRACK</li> </ul>
408	QUARTZ	TEST FOR HIGH SILANE CONCENTRATION AND LONG DURATION	9	268	NO	650	50	3	4	3	87.4	9.6	<ul style="list-style-type: none"> <li>QUARTZ LINER DID NOT CRACK</li> <li>FLOW WAS ADJUSTED EVERY HOUR TO MAINTAIN U/U<sub>mf</sub> = 4</li> </ul>
502	QUARTZ	SILICON PRODUCT- PURITY	11	260	YES	650	30	2.8	4	1.5	92.7	5.81	<ul style="list-style-type: none"> <li>PURE PRODUCT WAS PRODUCED</li> </ul>
503	QUARTZ	SILICON PRODUCT PURITY	11	267	PRODUCT OF RUN NO. 502	650	30	1.8	4	1.5	94	5.1	<ul style="list-style-type: none"> <li>PURE PRODUCT WAS PRODUCED</li> </ul>
X DATA WERE NOT RECORDED													



## SECTION IV

### EVALUATION OF VARIOUS ANALYTICAL TECHNIQUES

To establish the purity of silicon, involving metallic impurities in silicon in the ppba range, it is essential to have the measurements made with a reliable analytical technique by a commercial analytical laboratory with experience in analyzing silicon. Initially, atomic absorption, inductively-coupled plasma spectroscopy, neutron activation analysis (NAA), and spark source mass spectroscopy (SSMS) were selected as analytical techniques for evaluation. The first two analytical techniques suffer from an inherent drawback in that they require sample preparation by dissolving silicon in acids prior to analysis. This poses a serious problem to the analysis of metallic impurities in the ppba range because impurities will be diluted by at least a factor of 10 during sample preparation. Metallic impurities in silicon directly can be analyzed by NAA, and SSMS techniques and the dissolution of silicon samples is not required. For this reason, the SSMS and NAA techniques were finally selected to evaluate both these analytical techniques and the various commercial analytical laboratories that performed them.

Two different silicon samples were selected for evaluation of the analytical techniques:

- (1) The 111 to 508  $\mu\text{m}$  diameter silicon particles prepared at JPL by the previously discussed jet-milling and acid-cleansing techniques.
- (2) Komatsu silicon supplied by UCC. It is produced by the same procedure as is the high-purity Siemens silicon, except that the silicon rod is grown from the decomposition of silane instead of trichlorosilane. This semiconductor-grade Komatsu silicon rod was mechanically broken (UCC proprietary technique) into approximately 400  $\mu\text{m}$  diameter particles and the particles were used as a control sample for these evaluations.

For the SSMS analyses, identical samples were sent to the Northern Analytical Laboratory (NAL), Commercial Testing and Engineering (CT&E), and to the Wyoming Analytical Laboratory (WAL). For NAA, identical samples were sent to the Oak Ridge National Laboratory (ORNL), Activation Analyses (AA), and Lawrence Livermore Laboratory (LLL). The results are shown in Table 3. The data clearly indicate that measurements of the metallic impurities in an identical sample varies significantly from one type of analysis to another. Only the SSMS analysis, conducted by NAL, and the NAA analysis, conducted by ORNL, provided sensitivities consistent with the requirements.

#PRECEDING PAGE BLANK NOT FILMED

Table 3. Evaluation of Various Techniques for Analysis of Silicon

SAMPLE/VENDOR /TECH- NIQUES	-508 $\mu$ m PARTICLES JET MILLED AND ACID CLEANED FOR 10 min.					KOMATSU SAMPLE				
	NAL (SSMS)	CT&E (SSMS)	ORNL (NAA)	AA (NAA)	NAL (SSMS)	WAL (SSMS)	LLL (NAA)	ORNL (NAA)	AA (NAA)	
B	0.02	0.18			0.02	0.78	--			
P	0.1	1.0			0.1	0.36	--			
Fe	<0.5	<0.22	0.39	<5.5	<0.5	14.5	<5.6	0.004	<8.4	
Cr	$\leq$ 0.02	0.55	0.076	0.42	0.05	--	<0.11	0.00009	<0.079	
Ni	<0.3	--	0.0005	<2.21	<0.3	0.33	<0.29	0.0005	<3.6	
Cu	0.03	0.04	<0.06	<0.042	$\leq$ 0.02	0.13	<85.8	<0.04	<0.16	
Zn	<0.02	0.1	0.032	<0.51	<0.02	<0.17	<0.27	0.0024	<0.48	
Co	<0.1	0.01	0.0005	<0.02	<0.02		<0.012	0.0005	<0.07	
Ti	--	0.64	<2.8		<0.5	0.18	--	<2.8		
Mn	<0.02	0.02	0.01	0.035	<0.02	<0.05	--	0.00015	0.0075	
As	0.2	0.14	0.0004	<0.00324	<0.02	<0.05	<0.0048	0.00001	<0.0032	
Na	<0.1	1.0	1.2	1.3	<0.1	3.6	--	0.021	0.27	
Mg	<1	0.34			<1	12.7	--			
Al	0.05	0.18			0.1	0.1	--			
S	<1	1.3			<1	--	--			
Cl	10	4.5	0.79	<3.29	0.05	2.4	--	0.032	<0.64	
K	<0.07	0.79	0.086	<0.5	<0.07	10	--	0.029	0.15	
Ca	0.2	--			0.02	--	--			
Mo		$\leq$ 0.08	0.00015	<0.027	--	<0.12	<0.5	0.000015	<0.02	
Ga		0.14		<0.006		0.16			<0.003	
Li		0.032				8				
V		0.002	<0.0028				<0.025			
Zr		$\leq$ 0.018	<0.01					<0.006		
W			0.0092	0.0104				<0.000008		
Au				0.000031					0.000048	
Sb			0.00015					0.00004	0.00069	



## SECTION V

### RESULTS AND DISCUSSIONS

#### A. PERFORMANCE OF SILICON-SEED GENERATION DEVICE

The effectiveness of silicon grinding by the impingement of two opposing nitrogen jets was studied with respect to nitrogen-carrier flow rate with different initial silicon particle sizes. As shown in Figure 11, the average particle sizes of 600  $\mu\text{m}$  and 850  $\mu\text{m}$  (anticipated product sizes from a commercial reactor) were reduced to 330 and 430  $\mu\text{m}$ , respectively, after one pass-through at a nitrogen flow rate of 20 SCFM and a silicon feed rate of 48 gm/min. In another experiment, the one-pass yield for the desirable silicon-particle sizes of +75 to -355  $\mu\text{m}$  range (obtained from the feed size of +500 to 707  $\mu\text{m}$ ) was 15.8% at 12 SCFM  $\text{N}_2$  feed rate and 40 gm/min silicon feed rate. The two-pass yield increased to 28.3%. The effect of the silicon feed rate, shown in Figure 12, indicates that beyond the 100 gm/min silicon feed rate, further particle size reduction seems insignificant.

The combination of two possible mechanisms seems to control the nature of the silicon grinding brought about by the impingement of two opposing jets:

- (1) The chipping of a particle at the edges will produce very small size particles (1 to 30  $\mu\text{m}$ ) of approximately spherical shape.
- (2) The fracturing of flake-shaped particles produces smaller-size particles with the same flake-shape.

The silicon-grinding mechanism was verified by conducting a mass balance before and after the operation of the silicon seed generation device. It also was verified by examining the scanning electron micrographs of feed and product particles. Figure 13 indicates that the flake-shaped feed particles simply have been fractured into irregularly shaped smaller-sized flake-shaped particles. Particles with diameters less than 111  $\mu\text{m}$  were collected in the air bag filter. These particles were less than 1 wt % of the total silicon fed during one pass. This indicates that silicon grinding is mostly controlled by the second possible mechanism.

#### B. PERFORMANCE OF THE SILICON CLEANING DEVICE

To produce semiconductor-grade silicon particles, it is necessary to start with clean silicon seed material. The deposition of pure silicon via silane pyrolysis will dilute metallic impurities that already exist in the seed material, but will not be enough to produce pure silicon product. For this reason, silicon particles of less than 2 mm diameter were purchased from Dynamit Nobel with a minimum impurities level as indicated in Table 4 (e.g., Fe=20 ppma, Cr=0.5 ppma, Ni=10 ppma, Cu=0.06 ppma, Mn=0.5 ppma, and Al=2ppma). These particles are reduced to 200 to 300  $\mu\text{m}$  diameter by employing the seed-particle generation device and then are cleaned in the

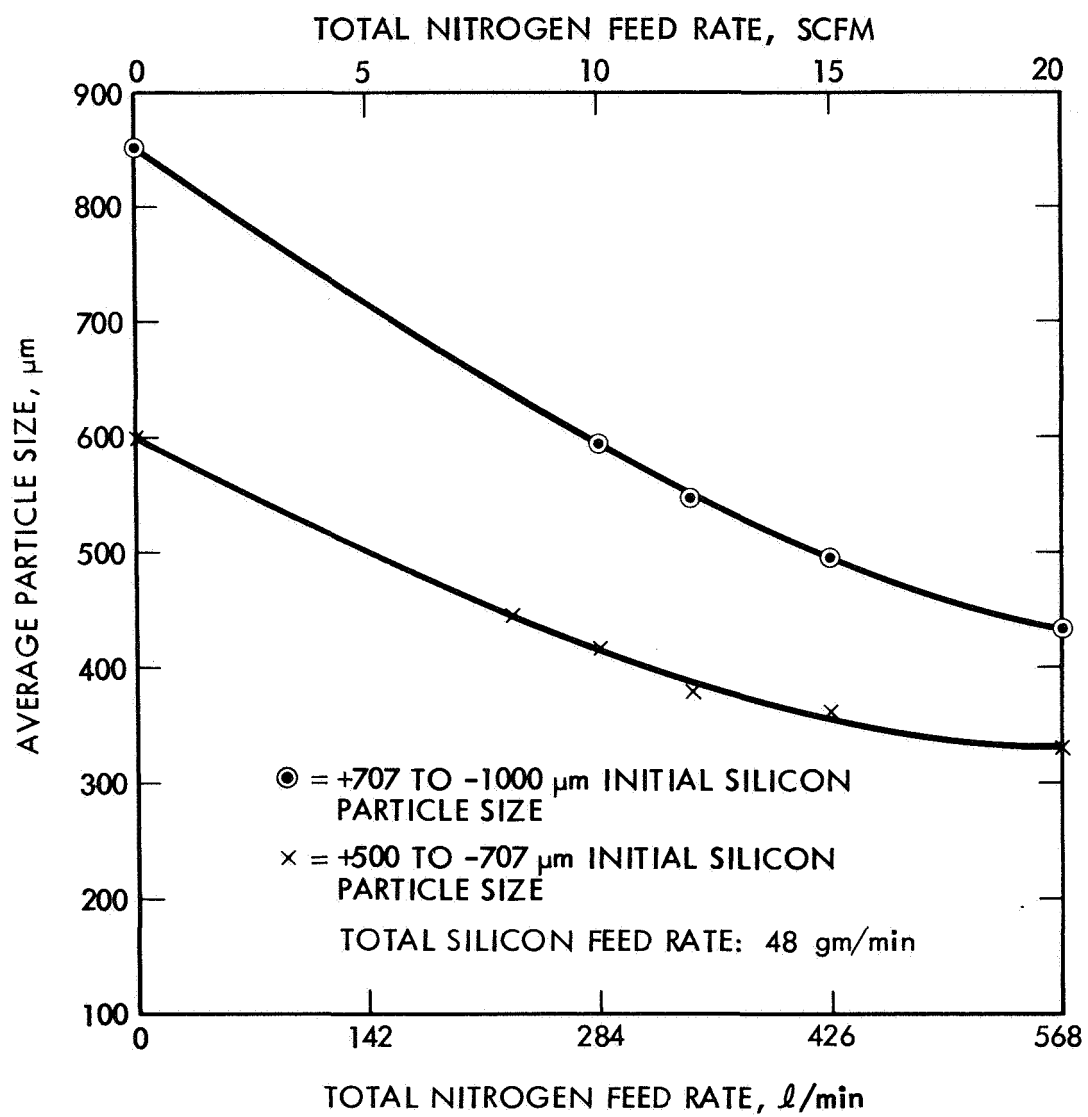


Figure 11. Effect of Carrier Gas Flow Rate on Jet Mill Grinding

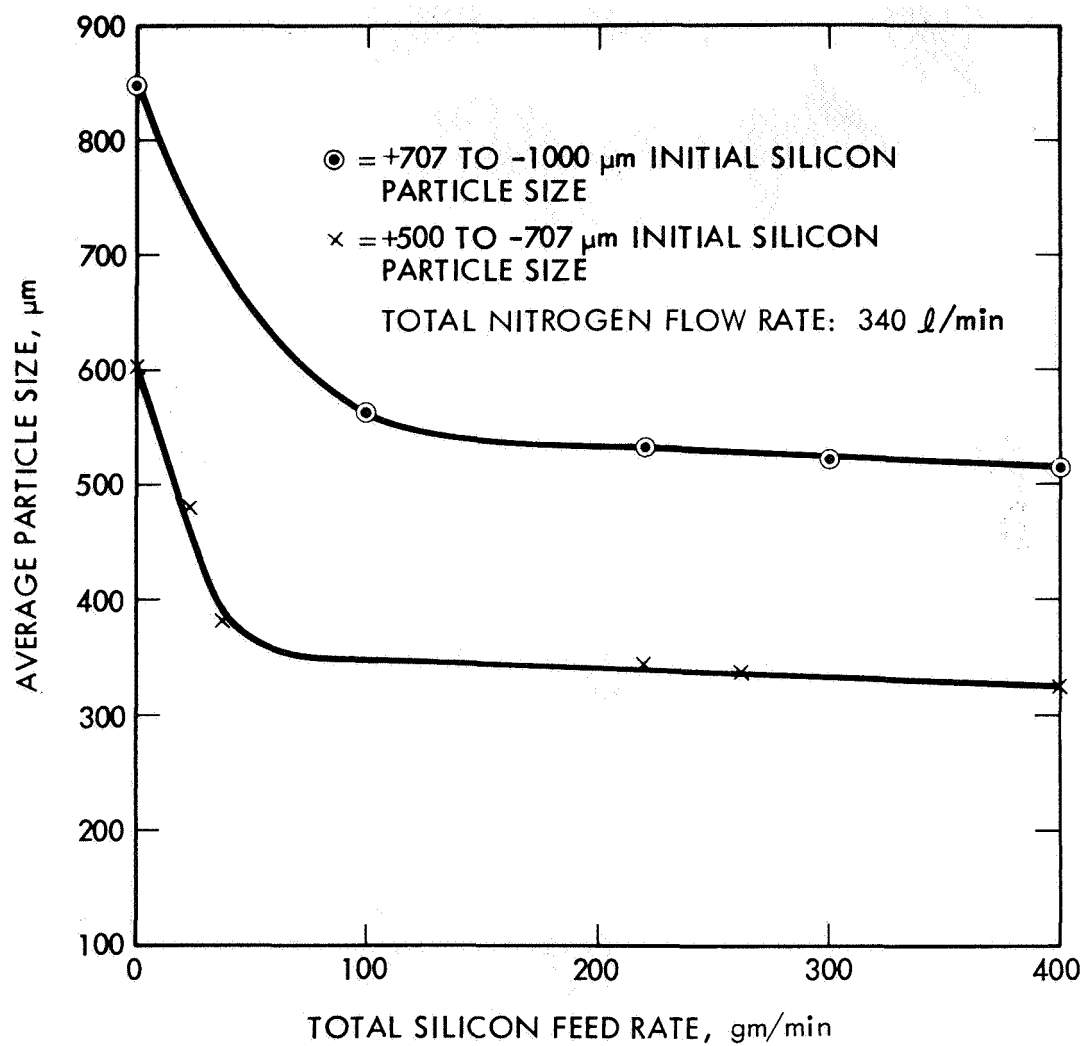


Figure 12. Effect of Silicon Feed Rate on Jet Mill Grinding



PRODUCT, 20x



FEED, 20x

NITROGEN FLOW RATE: 20 SCFM  
SILICON FEED RATE: 40 gram/min

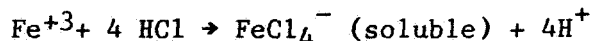
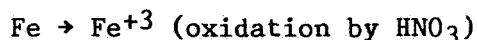
Figure 13. Scanning Electron Micrograph of Silicon Seed Particles from Seed Generation Device

ORIGINAL PAGE IS  
OF POOR QUALITY

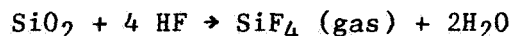
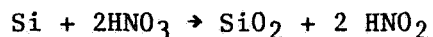
Table 4. Impurities in Acid-Cleaned Silicon Seed\* (ppma)

ELEMENTS	RAW PARTICLES "AS PURCHASED"	JET MILLED AND ACID CLEANED "SEED FOR FBR"
P	0.2	0.2
Fe	20	≤ 0.6
Cr	0.05	0.03
Ni	10	< 0.5
Cu	0.06	≤ 0.02
Zn	< 0.02	≤ 0.04
Co	≤ 0.1	≤ 0.1
Mn	0.5	≤ 0.02
Na	≤ 0.1	≤ 0.1
Mg	≤ 1	< 1
Al	2	0.05
S	< 1	< 1
K	≤ 0.07	< 0.1
Ca	0.6	0.1
* SPARK SOURCE MASS SPECTROSCOPY		

JPL-developed fluidized-bed silicon cleaning device. As indicated by the following equations, the mixture of  $\text{HNO}_3$  and  $\text{HCl}$  will remove metallic impurities as soluble chlorides:



The silicon oxide layer coating on the particle is removed by etching with concentrated  $\text{HF}$ .



The acid-cleaned particles have impurity levels below the detection limits of the spark source mass spectroscopy analytical technique as shown in Table 4 (e.g.,  $\text{Fe} < 0.6 \text{ ppma}$ ,  $\text{Ni} < 0.5 \text{ ppma}$ ,  $\text{Cu} < 0.02 \text{ ppma}$ , and  $\text{Mn} < 0.02 \text{ ppma}$ ).

#### C. PERFORMANCE OF THE SILICON WITHDRAWAL SYSTEM

The purpose of the withdrawal tube is selectively to take large particles out of the bed in a continuous or semicontinuous fashion. The results on withdrawal performance are shown in Figure 14. Half of the particles in the withdrawal boot have sizes greater than  $300 \mu\text{m}$ , although the average particle size in the bed is about  $220 \mu\text{m}$ . About 75% of the withdrawn particles are larger than  $200 \mu\text{m}$ . If economically necessary, the undersized particles (after product particle screening) can be recycled to the reactor for further growth. If 10% of the bed particles are withdrawn, the distribution ratio of  $400 \mu\text{m}$  particles in the withdrawal system compared to those in the bed is 1.4. In comparison, the distribution ratio of 1 represents almost uniform distribution of bed particles. Thus, this indicates that the selective withdrawal of larger particles takes place in the mildly fluidized column.

#### D. FLUIDIZED-BED REACTOR EXPERIMENTS

The experimental results from all key experiments (Series 200, 300, 400, and 500) are summarized in Table 2. Discussions of the most important results are presented in the following sections.

##### 1. Reactor Performance

The overall mass balance data are similar to those reported earlier (Reference 13). More than 90% of the total silicon fed into the reactor is deposited on the silicon seed particles, and the remaining 10% ended up as elutriated fines. The fines formation is influenced by the fluidization characteristics of the bed. If the bed is partially plugged, the fines formation are higher than 10% as in the case for Run. Number 202 and 203.

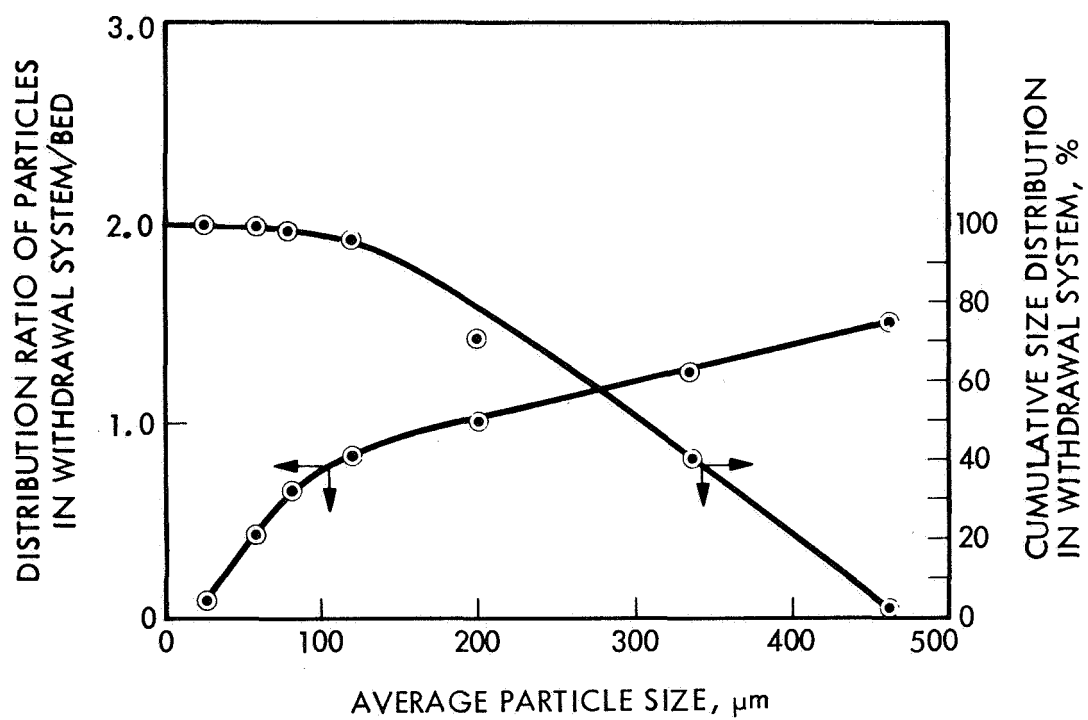


Figure 14. Performance of Silicon-Product Withdrawal System

The rate of silicon production is a function of silane concentration, seed particle size, and the U/U<sub>mf</sub> ratio. Figure 15 shows that in the 6-in. FBR, silicon production rates of 1.5 kg/h at 30% silane concentration, and 3.5 kg/h at 80% silane concentration, are achievable.

Most of the JPL experiments with the 6-in. FBR were of short duration (4 h). The particles were grown with deposition thicknesses of approximately 10 to 20  $\mu\text{m}$ .

Typical surface and deposition layer morphologies of the silicon products are shown in Figure 16. The SEM pictures show that the grown layer appears to be made up of small diameter particles with a large porosity or voidage.

## 2. Mechanism of Silicon Deposition

In an FBR, silane is decomposed and silicon is formed via two major paths (Figure 17):

- (1) Heterogeneous chemical vapor deposition (CVD) takes place on the surface of seed particles in the emulsion phase of the bed.
- (2) Homogeneous gas-phase pyrolysis occurs forming condensable silicon species in the bubble phase of the bed leading to the formation of nuclei (embryos). The general size of the initial embryos, according to nucleation theory, was estimated to be 50 Å. (JPL IOM CP-381-76-31), Hsu/Praturi to Lutwack, "Application of Nucleation Theory to Silicon Seed Growth," March 1976).

The tiny silicon nuclei move about within the bubbles by Brownian motion and fuse by the action of van der Waals forces (path 3 in Figure 17). According to Levenspiel (Reference 14), the growth rate of a nucleus with a radius  $r$ , in this regime, is found to be:

$$\frac{dr}{dt} = \left( \frac{2kTf_s}{3\pi\mu} \right) \frac{1}{r^2}$$

where:

$k$  is the Boltzmann constant

$\mu$  is the viscosity of a nucleus in the gas stream

$f_s$  is the volume fraction of solids in the gas-solids mixture

$T$  is temperature in °K.

By the time it takes nuclei to grow to 0.3  $\mu\text{m}$  size (<0.1 s), the nuclei are so few and far between (from the standpoint of Brownian Motion) that the growth rate drops by a factor of  $10^{-4}$ . The mass of fine particles that results at this stage of nuclei coalescence is called coccal silicon. As a result of bubble distortion and the kneading action of fluid eddies in the fluidization medium, these coccal silicon fines may come out of the gas bubble into the emulsion phase.



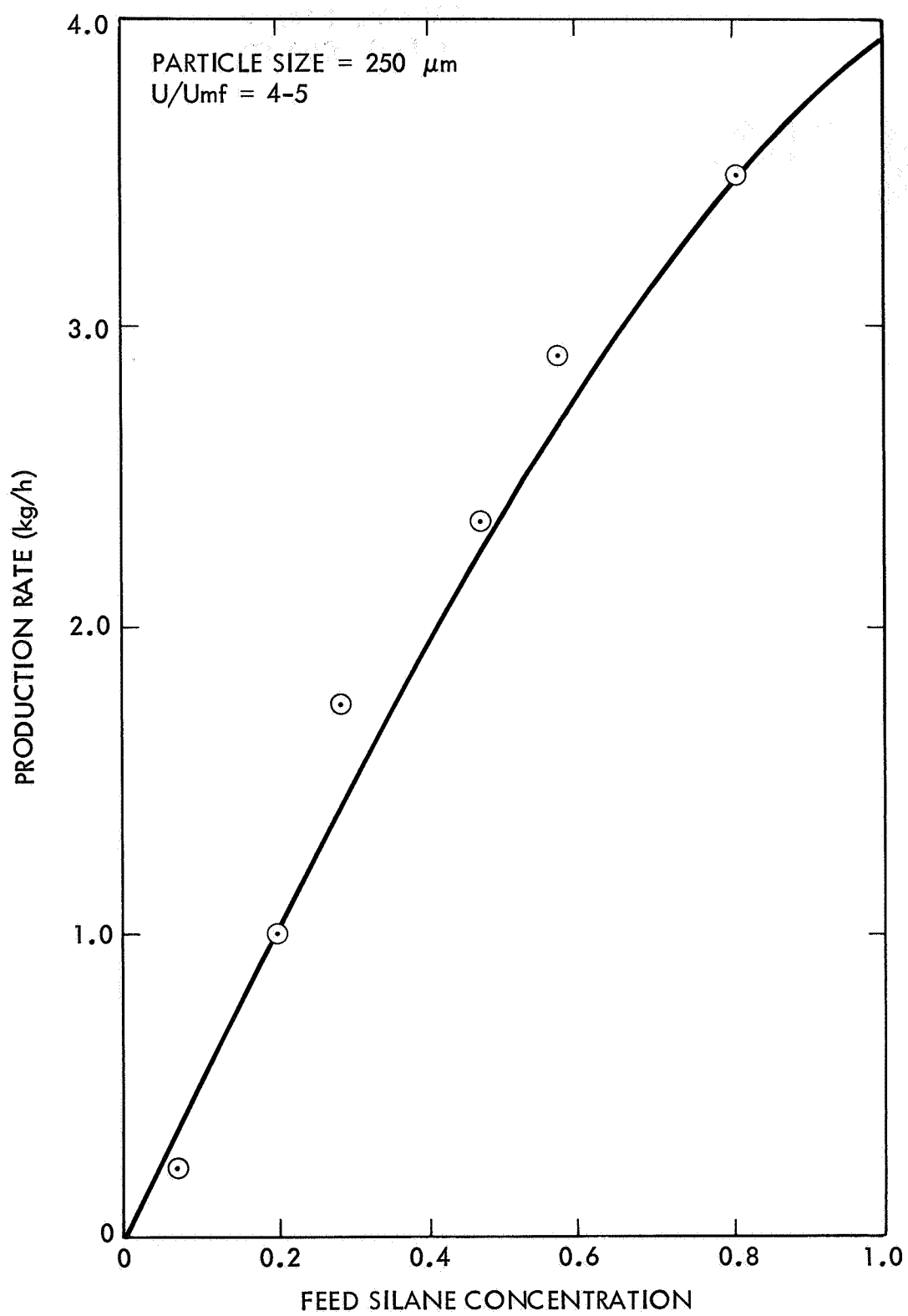


Figure 15. Experimental Silicon Production Rate Versus Silane Concentration

ORIGINAL PAGE IS  
OF POOR QUALITY

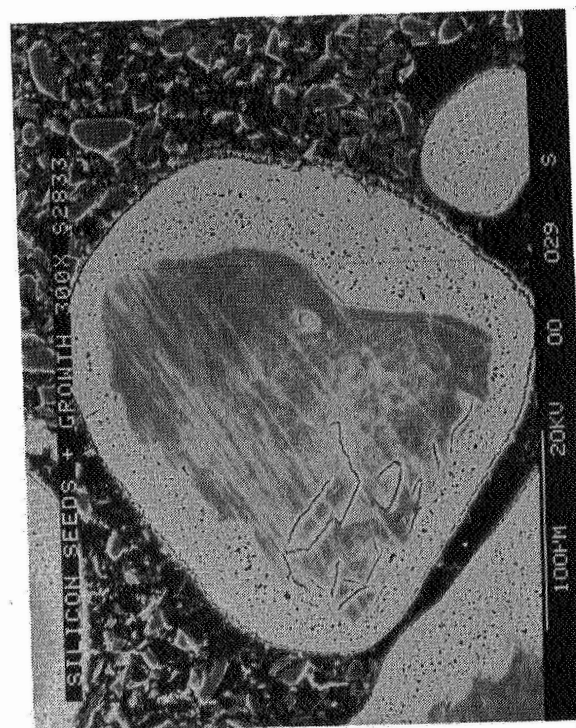
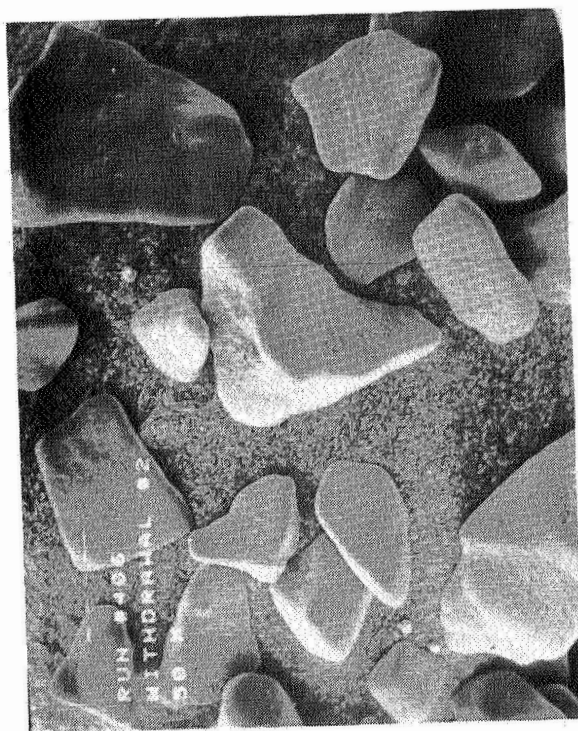
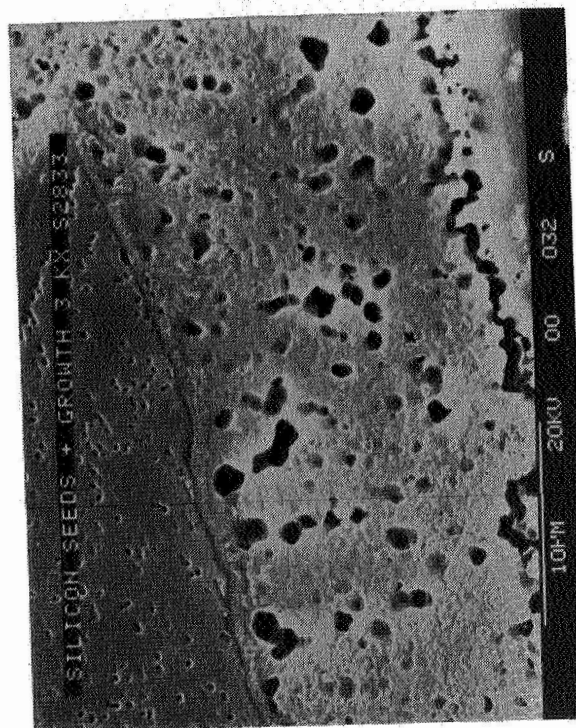


Figure 16. Scanning Electron Micrographs of the Silicon Product from a Fluidized-Bed Reactor (659°C, 30% SiH<sub>4</sub>, 4 h)  
Deposition  $\approx 17 \mu\text{m}$

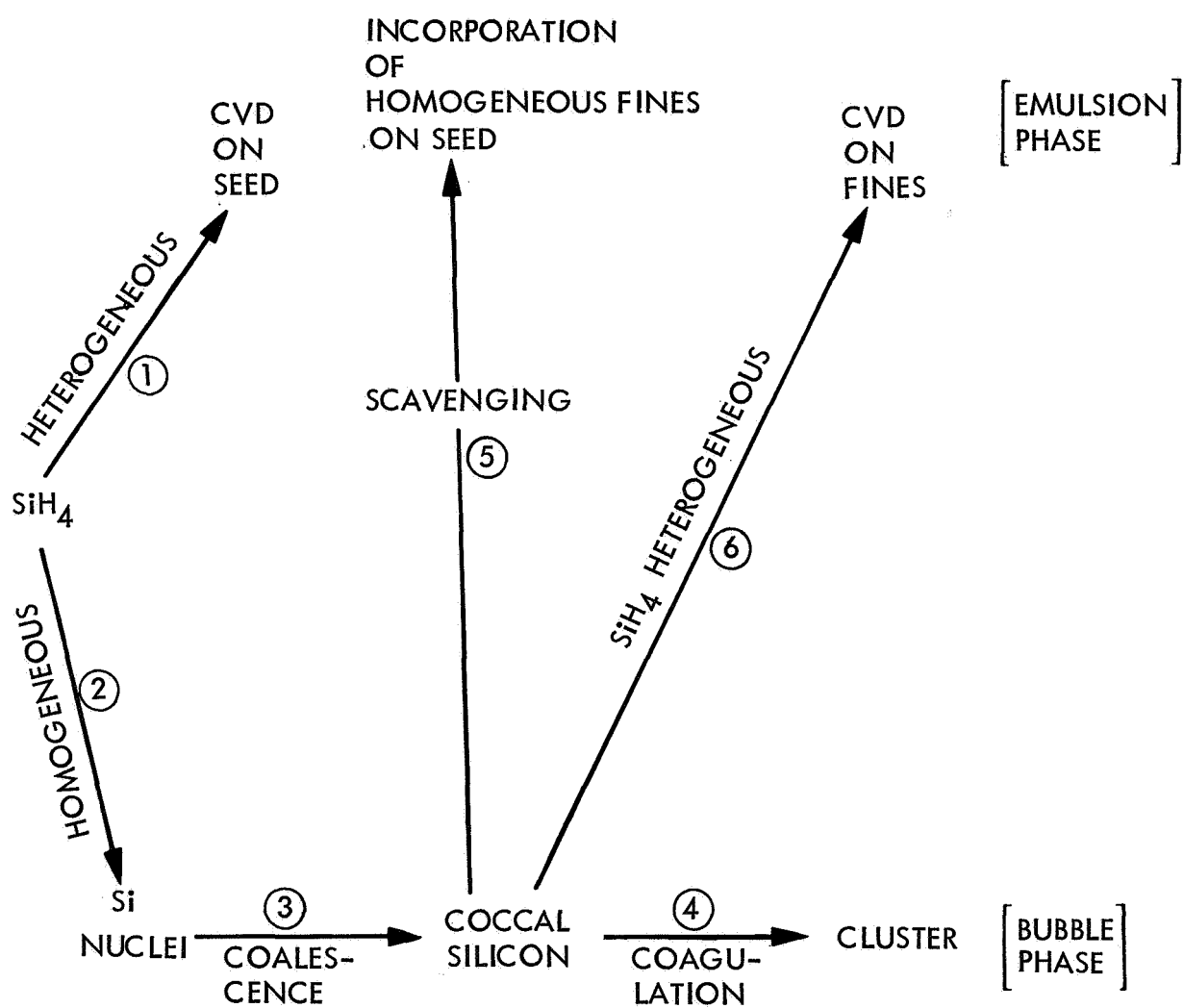


Figure 17. Reaction Paths for Silane Pyrolysis in a Fluidized-Bed Reactor

Within the bubbles, the coccal silicon fines coagulate into clusters. The size or length of a cluster grows as the residence time of the bubble in the bed increases. Since coagulation is a consequence of solid particle collision, the product is not densely packed. The resulting cluster is light in density and travels with the gas bubble. At the top of the bed, bubbles burst and a fraction of the silicon, typically <10% of the silicon input in the forms of clusters and residual coccal silicon fines, is elutriated and collected in the exit filter. Limited by the terminal velocity of the operation of the fluidized bed, the maximum size of the elutriated clusters is about 10  $\mu\text{m}$  under these experimental conditions.

In the emulsion phase, the seeds sweep up the fine particles made up of both coccal silicon and initial clusters released from the bubbles. This phenomenon is called scavenging and has been reported in the FBR-literature as an effective means for the removal of fine particulates in gas-solid fluidized beds (References 15,16).

Based upon our data, it appears that the following criteria must be met to incorporate fines:

- (1) The temperature of the scavenging region must be higher than the Tammann temperature<sup>2</sup> of silicon (defined as 0.52 times the melting point of silicon in  $^{\circ}\text{K}$ ). This threshold temperature is  $610^{\circ}\text{C}$ , or  $40^{\circ}\text{C}$  below the  $650^{\circ}\text{C}$  empirically-determined, optimum operating temperature of the FBR. It represents the minimum seed-particle surface temperature required to incorporate fines. As shown by SEM pictures in earlier work (Reference 17), scavenging of fines at temperatures below the Tammann temperature leads only to loose adhesion.
- (2) The CVD reaction serves to cement the homogeneous fines into the growth. This surface adsorption of homogeneously nucleated particles and simultaneous heterogeneous deposition is similar to the model proposed in the carbon deposition literature (References 19,20).
- (3) Fines, mostly coccal silicon, grow by heterogeneous chemical vapor deposition in the emulsion phase as represented by path 6 in Figure 17. Because the rate of scavenging by the silicon seeds is relatively fast and the surface area of coccal silicon versus that of the seed particles is small, the CVD growth of coccal silicon is generally considered to be an unimportant deposition process.

### 3. Product Morphology

To determine product morphology, the fluidized bed fines and product-silicon particle samples were mounted in resin and (1) ground, (2) ground and etched, (3) polished, and (4) polished and etched before SEM

---

<sup>2</sup>Tammann temperature is an index for surface mobility. It is the minimum temperature at which a solid undergoes solid-solid interactions such as a transformation from a non-wetting to a wetting condition (Reference 18).

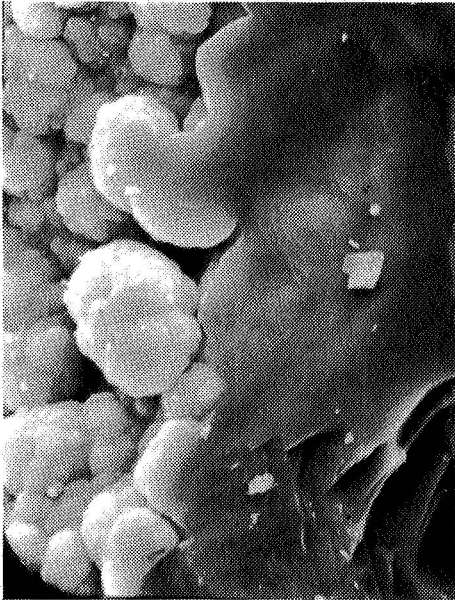
examination. Etch compositions used were the Sirtl, Dash, and a proprietary Schwuttke formulation (personal communication, G.H. Schwuttke). The x-ray diffraction method was used to ascertain the structure of the product and the fines. Sharp lines confirmed the crystallinity of both. The samples evaluated were produced in runs in which the feed gas composition ranged from 6.24%  $\text{SiH}_4$  in  $\text{H}_2$  to pure silane. Bed temperature was controlled at 650°C for all feed gas concentrations except the lowest concentration of 6.24%. The latter was run at 920°C.

The surfaces of the product particles are characterized by a coating of 0.1 to 4  $\mu\text{m}$  diameter particles and continuous nodular growth features: 15–20  $\mu\text{m}$  diameter nodules are observed in the sample deposited at 920°C (Figure 18a). The nodules propagate outward from the surface of the growing layer. The spacing between the nodules extends downward as continuous pores or channels into the deposited layer. A fractured cross-section of the product particles shows the nodules to be continuous with the grown layers (Figure 18b). The cross-section also reveals that the continuous porosity in the grown layer decreases from the particle surface inward toward the grown-layer/seed interface. The channel diameter is smaller (typically  $<1\ \mu\text{m}$ ) near the particle surface, and larger (1.5 to 2  $\mu\text{m}$ ) further into the deposited layer. The walls of the channels also exhibit the nodular growth habit (Figure 18c). In some samples, the dense bulk of the deposited layer reveals no apparent structure as cleaved (Figure 18b), while in others a granular structure is revealed by a more dispersed reflectivity. When etched with Dash etch, the deposited layers appear to be made up of 0.1 to 0.2  $\mu\text{m}$  diameter particles cemented together. The Schwuttke etch also reveals 0.2  $\mu\text{m}$  diameter particles in the channel walls. A distinct discontinuity occurs at the seed/grown-layer contact (Figure 18c). None of the seed structure propagates into the deposited material. Etch rates at the contact are exaggerated. Nearly continuous horizons of pores parallel to the original seed surface are occasionally observed in the deposited material suggesting an interruption and subsequent resumption of the deposition process.

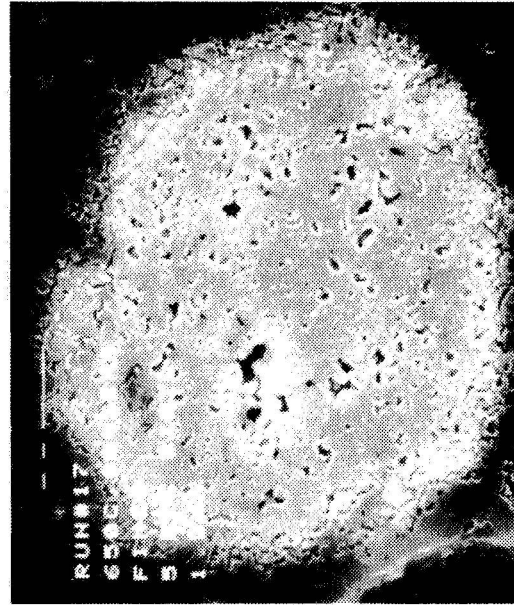
The appearance of the surface of the fines is the same as that of the deposited layers on the seeds (Figure 18d). A sample of fines was mounted, lapped, polished and etched for 5 s in a standard Sirtl etch. After etching, the sample was identical in appearance to growth areas on the seed material. The sample is porous with the matrix between the holes appearing to be made up of particles 0.2 to 0.4  $\mu\text{m}$  in diameter. The size of the fines ranged from 5 to 15  $\mu\text{m}$  in diameter. Approaching the particle surface, the pores in the fines sample increased in number and decreased in diameter. In one analyzed sample, the largest pore, 6  $\mu\text{m}$  in length x 1.5  $\mu\text{m}$  in width, was near the center. The average diameter of the pores is about 1.5  $\mu\text{m}$  near the surface of the sample.

The continuity of the nodular growth with the grown layer supports the conclusion that the surface features are the products of a heterogeneous nucleation and deposition process. That the bulk of the grown layer appears to be made up of small diameter particles supports the concept of scavenging of homogeneously nucleated material. Thus, to explain all the textures observed, the concept can be invoked of particle capture with subsequent cementation and nodular growth.

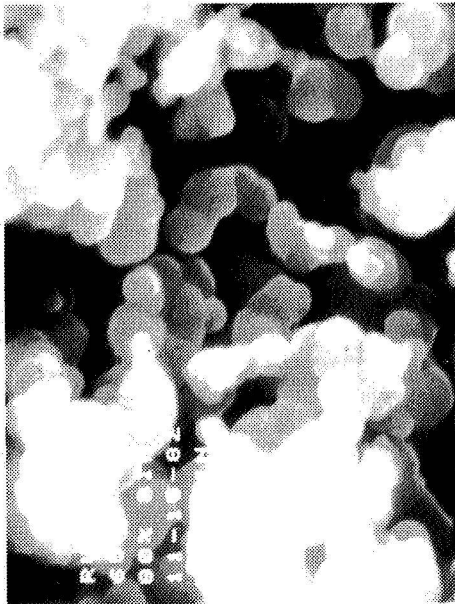
ORIGINAL PAGE IS  
OF POOR QUALITY



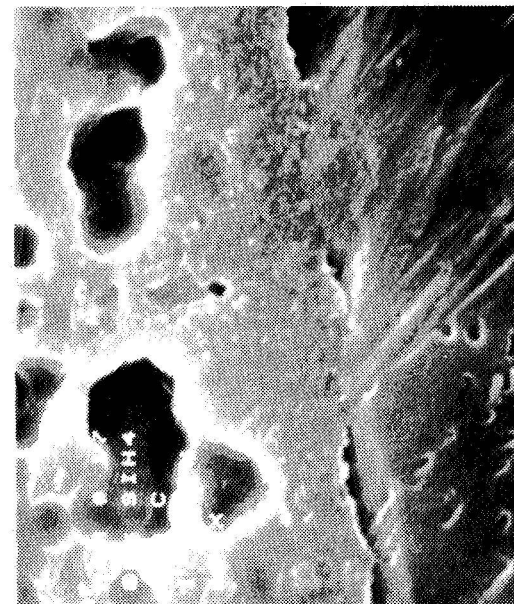
(b) PRODUCT



(d) FINES



(a) PRODUCT



(c) PRODUCT

Figure 18. Morphology of Deposited Layer of Silicon and the Elutriated Fines

#### 4. Experiments for Further Control of Fines Formation

A small portion of homogeneous nuclei formed from the silane pyrolysis is not scavenged by the seed particles and escapes the bed as fines. This partly may be caused by the unavailability of silane at the top of the bed to cement the absorbed homogeneous nuclei by chemical vapor deposition. A series of experiments was run to demonstrate that:

- (1) Fines formation can be reduced further by providing added cementation by a secondary source of silane admitted at a suitable bed location.
- (2) The scavenging phenomenon does exist under fluidized-bed conditions.

An ideal bed height of 8 in. was calculated to be necessary for 99% of the silane to react. This calculation is based on published homogeneous (Reference 21) and heterogeneous (Reference 22) rate constants, and the reactor conditions of 650° bed-temperature, 50% primary silane feed and a total volumetric flow rate of 40 l/min. A 50% increase in reaction length was assumed because of the non-ideality of the fluidized bed. This resulted in an actual 99% reaction-length of 12 in. The secondary silane injection point was located 13 in. above the distributor (Figure 2). Total static bed depth was 25 in. Based on the cluster growth rate equation (Reference 17), the cluster size is calculated to be approximately 0.8  $\mu\text{m}$  at the 13 in. level above the distributor.

Control and scavenging experiments were conducted using the reactor conditions given above. A bed height of 25 in. was used to allow for secondary scavenging of silicon clusters. The secondary silane injection for the control run consisted of 12 l/min of hydrogen. Two l/min of silane and 8 l/min of hydrogen were used in the scavenging experiment. The data are shown in Table 2 as Run Numbers 204 and 206, and in Table 5. The data indicate that the elutriated fines were reduced from 10% (control) to 6% (scavenging) with a corresponding increase in silicon deposition efficiency in the bed from 92 to 95.5%. The particles of less than 75  $\mu\text{m}$  in diameter were increased by 0.1% in the control experiment, while they were reduced by 1% in the scavenging experiment. The product morphology studies, and these experiments, strongly support the proposed silicon-deposition mechanisms.

#### 5. Performance of a Quartz Liner

The performance of a quartz liner mounted inside the stainless steel reactor was evaluated based on the following criteria:

- (1) The time required to reach a steady-state bed temperature of 650°C, when an 11 kg batch of 250  $\mu\text{m}$  average diameter silicon particles is fluidized with hydrogen at a  $U/U_{mf}$  ratio of 4 (Table 2, Run Number 300).
- (2) The maintenance of the bed temperature during pyrolysis using 50% silane in hydrogen (Table 2, Run Numbers 402, 406 to 408).

Table 5. Scavenging Effect of a Secondary Silane Injection

	CONTROL RUN	SCAVENGING RUN
PERCENTAGE AS FINES VERSUS FEED Si	10%	6%
FINE PARTICLES IN THE BED (-75 $\mu\text{m}$ ):		
PERCENTAGE IN THE SEED	5%	2.6%
PERCENTAGE DIFFERENCE IN PRODUCT VERSUS SEED	0.1%	-1%
PERCENTAGE OF PRODUCT IN BED	92%	95.5%
PRODUCTION RATE (kg/h)	1.3	1.5



- (3) The maintenance of the proper bed-temperature profile necessary to eliminate deposition of silicon on the inside quartz liner wall. If this parameter is not properly established, the quartz liner will break during thermal cycling due to the differential thermal expansion between quartz and silicon.

It takes approximately 3 h to reach the steady-state bed temperature of 650°C. This is about 1 h longer than is required if silicon is directly heated through the stainless steel wall (no quartz liner). Once the required bed temperature is reached, however, its maintainability is fairly good, and is complemented by the exothermic reaction (-5 kcal/mole) of the silane pyrolysis.

The bed-temperature profile is shown in Figure 19. Bed temperatures are 400°C and 650°C at 1/2 in. and 2 in. from the gas distributor, respectively. The temperature of the outer wall of the quartz liner was within 5°C higher than the bed temperature. This temperature profile is very desirable because it facilitates deposition of silicon on the seed particles, but not on the liner wall. During our experiments, quartz liners were exposed to silane pyrolysis at 650°C for a duration of up to 4 h. The quartz liner did not crack 90% of the time. No silicon deposition was found on either the inside or the outside of the liner wall.

The silicon mass balance data, involving both silicon in the bed and elutriated as fines, were similar to the ones obtained using no quartz liner (Table 2, Run. Numbers 406 to 408).

## 6. Product Purity

The purity of the FBR product was determined for two cases:

- (1) The FBR was operated without a liner, and silicon particles were exposed to the hot, stainless steel-reactor wall.
- (2) The FBR was operated with a quartz liner. This isolates the silicon particles from the stainless steel-reactor wall.

For the non-liner case, the concentrations of metallic impurities in the FBR product are shown in Table 6. These data indicate that the silicon product is heavily contaminated with metallic impurities. The iron, chromium, and nickel impurities are approximately 70, 17, and 12% of the total identified impurities. Interestingly, these proportions are similar to the composition of the stainless steel 316 reactor-wall material. It is evident, therefore, that hot silicon particles physically removed the stainless steel wall materials and the metallic impurities are incorporated onto the seed silicon during the silane pyrolysis.

For the case with the quartz liner, the metallic impurities in the FBR product are shown in Table 7. The use of a quartz liner as a barrier between the silicon particles and the stainless steel reactor wall helped to eliminate metallic contamination in the product silicon during fluidized-bed processing. The metallic impurities in the product silicon generally are less

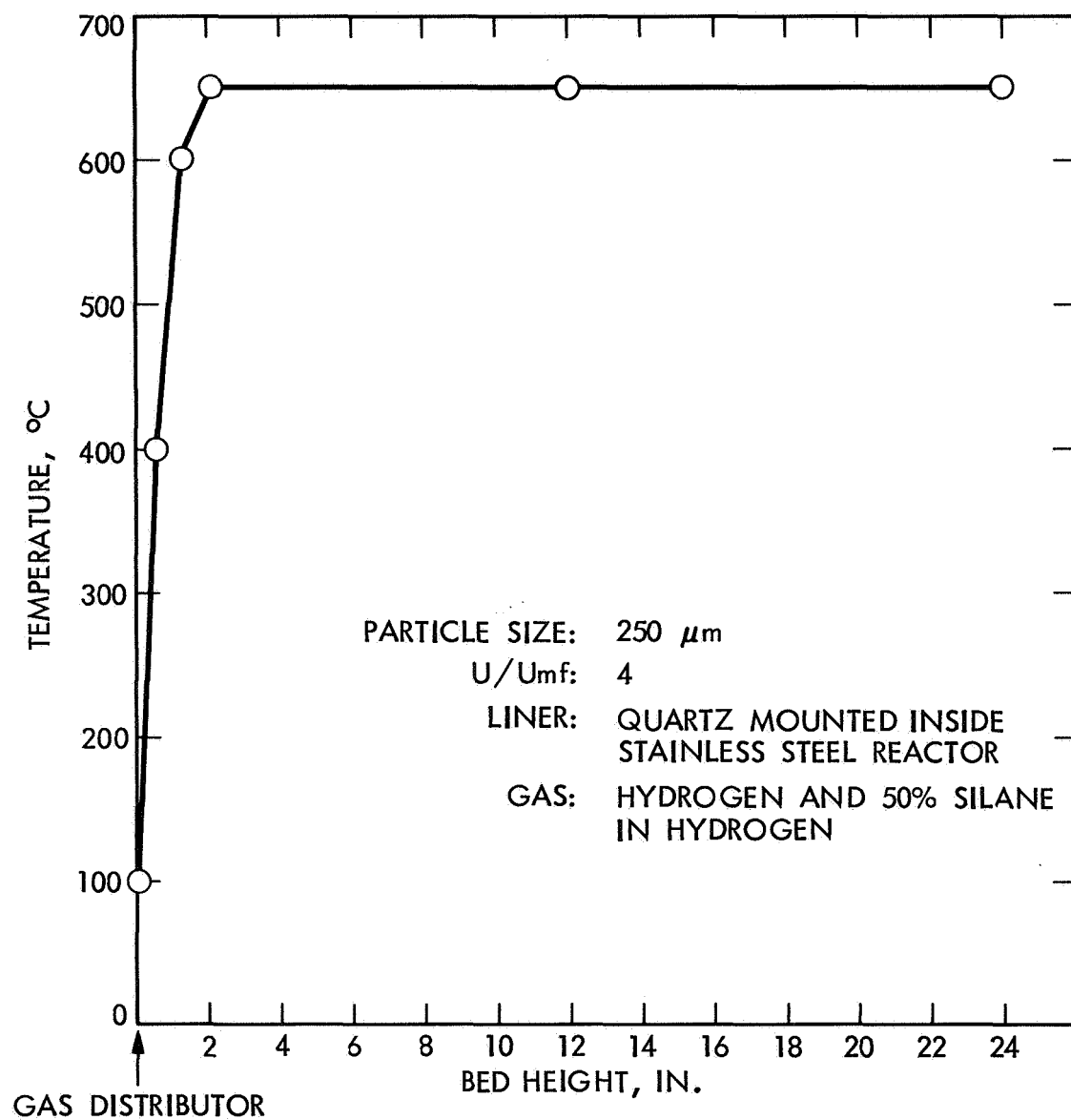


Figure 19. Temperature Profile in 6-in. Fluidized-Bed Reactor Fitted with Quartz Liner

than the detection capability limits of spark source mass spectroscopy. The purity of the deposited layer of silicon is equal to or better than that of the starting silicon seed material.

## 7. Solar Cells

For both the non-liner and quartz liner cases, a Czochralski (CZ) single-crystal ingot was pulled and sliced to fabricate 2 x 2 cm baseline solar cells. For the case without the quartz liner, the ingot size is 4-in. diameter x 2-in. high (Figure 20). The resistivity of wafers obtained from this ingot is 1.98  $\Omega$ -cm at the top and 1.83  $\Omega$ -cm at the bottom. The performance data of these cells are shown in Table 8. The average efficiency of these undoped antireflective (AR) coated solar cells is 12.1 to 12.5% compared to the 13.9% obtained by using semiconductor-grade silicon of 2  $\Omega$ -cm resistivity.

For the case with the quartz liner, the ingot size is 2-in. diameter x 3-in. high (Figure 21). The 18 mil wafers prepared from this ingot have resistivities varying from 23 to 34 ohm-cm. The oxygen and carbon impurities are 11.6 and 7.4 ppma, respectively. X-ray diffraction analysis shows this ingot has a single crystal structure and orientation of [100] type. The performance data of the 2 x 2 cm cells prepared from this material are shown in Table 9. The average efficiency of these undoped AR coated solar cells is approximately 11 to 12%. The control solar cells from 30  $\Omega$ -cm semiconductor-grade silicon were not prepared.

Table 6. Purity of Product from a Fluidized-Bed Reactor not Equipped with a Liner (ppmw) (Neutron Activation Analysis - Lawrence Livermore Laboratory)

JPL RUN No.	Cr	Fe	Ni	Co	Mo	W	Na	TOTAL IDENTIFIED
111 (SEED)	4		1		0.05	0.04	1.3	
111-4P <sup>1</sup>	16 (15%)	77 (72%)	11 (11%)	0.16	0.76 (0.7%)	0.1	2	107
111-8P <sup>2</sup>	45 (17%)	185 (70%)	31 (12%)	0.36	3.8 (1.4%)	0.15	1.3	266
115P <sup>3</sup>	46 (17%)	197 (71%)	30 (11%)	0.4	1 (0.4%)	0.1	1.1	275
115 INGOT - BOTTOM	0.7						1.3	
115 INGOT - MIDDLE	0.2						4.2	
115 INGOT - TOP	0.3						1.2	
<p>REACTOR WALL MATERIAL: STAINLESS STEEL 316: Cr 17%, Fe 70%, Ni 12%, Mo 2.5%, Mn 2%, Si 1%  FOR EXPERIMENTAL CONDITIONS FOR RUN NO. 111 AND 115, REFER TO REPORT (REFERENCE 26).</p> <p><sup>1</sup> 4P IS PRODUCT OBTAINED AFTER 4 h  <sup>2</sup> 8P IS PRODUCT OBTAINED AFTER 8 h  <sup>3</sup> P IS FINAL SILICON PRODUCT</p>								

Table 7. Purity of Product from a Fluidized-Bed Reactor Equipped with a Quartz Liner (ppma)

ELEMENTS	JET MILLED AND ACID CLEANED SEED FOR FBR	FBR PRODUCT <sup>1</sup>
	SSMS <sup>2</sup>	SSMS
P	0.2	0.1
Fe	≤ 0.6	≤ 0.6
Cr	0.03	< 0.02
Ni	< 0.5	< 0.5
Cu	≤ 0.02	< 0.02
Zn	≤ 0.04	< 0.04
Co	≤ 0.1	≤ 0.1
Mn	≤ 0.02	< 0.02
Na	≤ 0.1	≤ 0.1
Mg	1	< 1
Al	0.05	0.05
S	< 1	< 1
K	< 0.1	< 0.1
Ca	0.1	0.1
<sup>1</sup> RUN NO. 502 AND 503		
<sup>2</sup> SPARK SOURCE MASS SPECTROSCOPY CONDUCTED BY THE NORTHERN ANALYTICAL LAB		

ORIGINAL PAGE IS  
OF POOR QUALITY

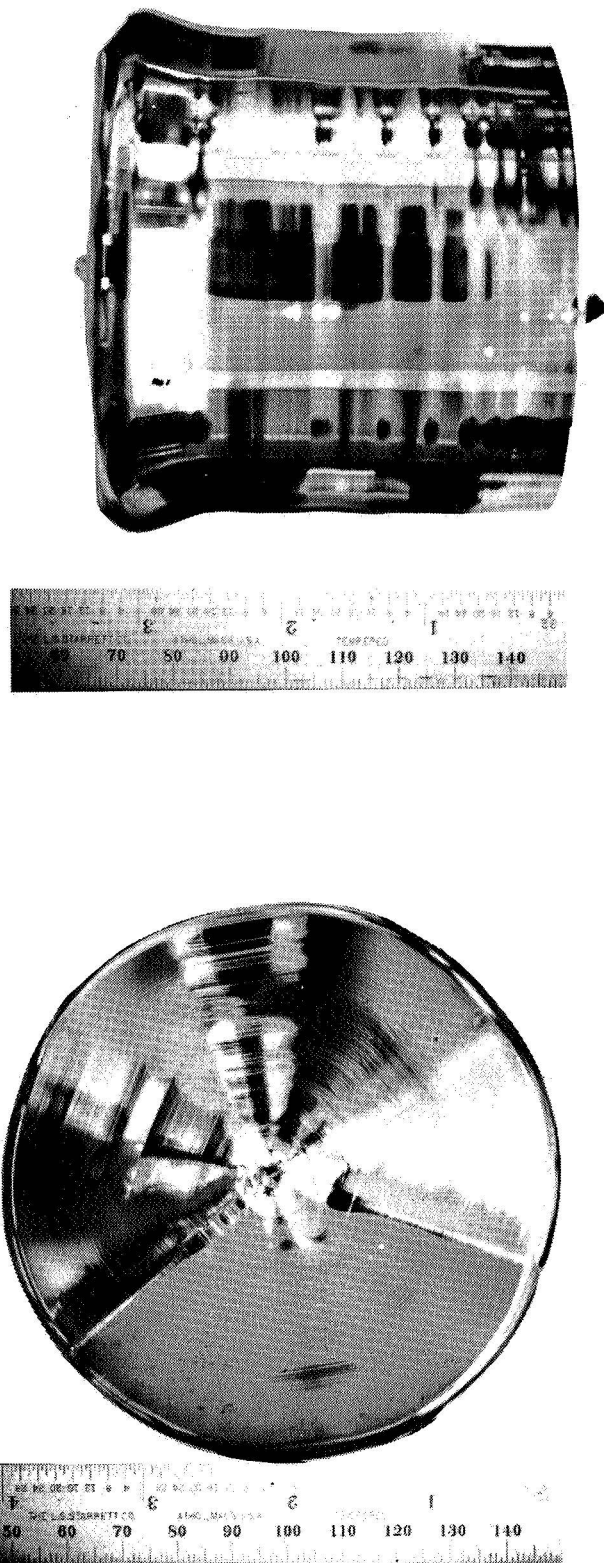


Figure 20. Czochohalski Ingot from a Fluidized-Bed Reactor Product, JPL Run 115

Table 8. Performance of Solar Cells\* Fabricated from the Silicon Produced in a Fluidized-Bed Reactor not Equipped with a Liner

SILICON TYPE	RESISTIVITY (ohm-cm)	V <sub>OC</sub> (mV)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	CFF (%)	η (%)
TOP-INGOT RANGE (AVERAGE)	1.91	570 564 - 574	28.7 27.5 - 29.5	76 73 - 78	12.5 11.7 - 12.9
MIDDLE-INGOT (AVERAGE)	1.83	565	28.9	74	12.1
BOTTOM-INGOT (AVERAGE)	1.83	567	27.9	77	12.2
Cz INGOT CONTROL (SEMICONDUCTOR-GRADE SILICON)	-	586	30.7	77	13.9
* BASELINE CELLS, 2 x 2 cm AR COATED.					

ORIGINAL PAGE IS  
OF POOR QUALITY

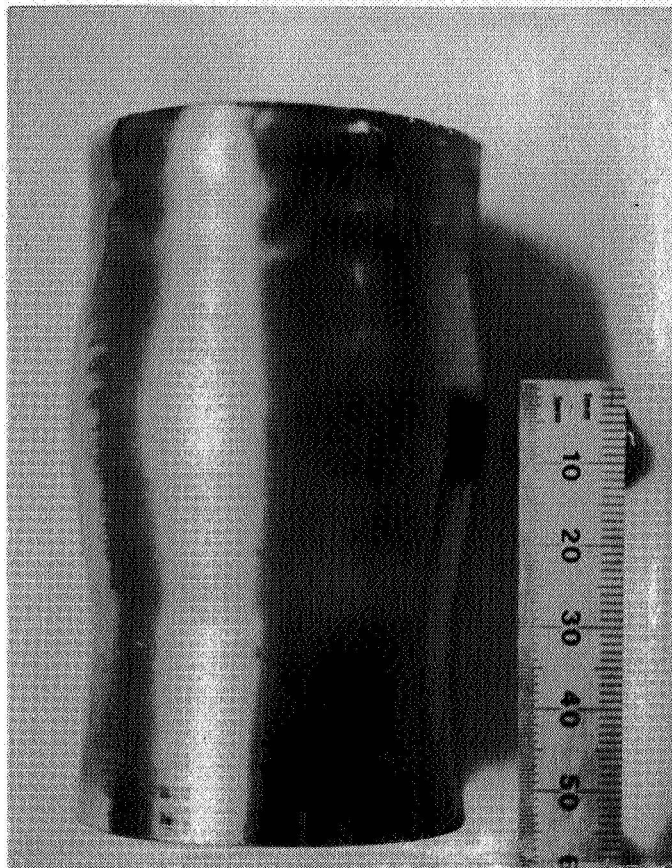


Figure 21. Czoehralski Ingot from a Fluidized-Bed Reactor  
Product, JPL Run 503



Table 9. Performance of Solar Cells\* Fabricated from the Silicon Produced in a Fluidized-Bed Reactor Equipped With a Quartz Liner

SILICON TYPE	RESISTIVITY (ohm-cm)	V <sub>OC</sub> (mV)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF (%)	η (%)
TOP 0 TO 1/2 IN. PORTION OF INGOT	34.2	532.8 - 535.1	27.95	0.77	11.37 - 11.55
TOP 1/2 TO 1 IN. PORTION OF INGOT	28.17	526 - 537.5	27.95	0.76	10.9 - 11.52
TOP 1 TO 1-1/2 IN. PORTION OF INGOT	23.25	523.2 - 536.5	27.95 - 28.55	0.74	10.87 - 11.36
TOP 1-1/2 TO 2 IN. PORTION OF INGOT	33.11	537.6 - 542.3	27.38 - 28.1	0.77	11.4 - 11.6
* BASELINE CELLS, 2 x 2 cm AR COATED.					



## SECTION VI

### CONCLUSIONS

The following conclusions are drawn from the recent FBR experimental work:

- (1) Silicon-seed particles can be prepared from 2 mm silicon particles by using the JPL-developed seed-generation device. A one-pass yield of 15.8% (-75 to +355  $\mu$ m particle diameter) has been achieved.
- (2) Because the prepared seed particles require cleaning, a fluidized-bed, silicon-seed cleaning device has been developed and the purity of the seed particles has been established.
- (3) The mechanism of the deposition of silicon from the pyrolysis of silane in an FBR is described by a six-path process: heterogeneous deposition, homogeneous decomposition, coalescence, coagulation, scavenging, and heterogeneous growth on fines.
- (4) The scavenging of homogeneously nucleated silicon by silicon particles was experimentally achieved by using a secondary silane injection.
- (5) The selective removal of large particles of product silicon has been demonstrated.
- (6) It has been demonstrated that more than 90% of the silicon fed to the reactor is deposited on the silicon seed particles. Less than 10% of the silicon feed ends up as elutriated silicon fines.
- (7) The beneficial performance of a quartz liner in an FBR is established. With operating conditions defined (temperature, profile, etc.), the quartz-lined FBR was successfully operated at up to 50% silane concentration for a duration of 4 h.
- (8) The purity of the silicon produced in a quartz-lined FBR was established. The metallic impurities are less than the detection limits of spark source mass spectroscopy.
- (9) Solar cells fabricated from the silicon produced in a FBR with no quartz liner had an efficiency of approximately 12.5% and a resistivity of 2 ohm-cm.
- (10) Solar cells fabricated from the silicon produced in a quartz-lined FBR had a resistivity of 23 to 34 ohm-cm and an efficiency of approximately 11 to 12%.

PRECEDING PAGE BLANK NOT FILMED



## SECTION VII

### RECOMMENDATIONS

Although the JPL in-house research program demonstrated a better understanding of the fluidized-bed silane process, the following engineering problems remain to be solved:

- (1) How to operate an FBR for a long duration to reach a steady-state with respect to the particle-size produced. In this mode, seed particles of 200  $\mu\text{m}$  diameter would be fed continuously to the FBR and product particles of 1 mm diameter would be withdrawn continuously from the FBR.
- (2) A demonstration is needed that the silicon product produced in the FBR is of semiconductor-grade.
- (3) A pilot-plant demonstration of the FBR process is needed.

**PRECEDING PAGE BLANK NOT FILMED**



## SECTION VIII

### REFERENCES

1. DOE/JPL Low-Cost Solar Array Project Annual Operating Plan for Fiscal Year 1980, JPL Document 5101-127, Jet Propulsion Laboratory, Pasadena, California, August 31, 1979.
2. "National Photovoltaics Program Five Year Research Plan, : 1984-1988; Photovoltaic Energy Technology Division, U.S. Department of Energy, Washington, D.C., May 1983.
3. Lutwack, R. "A Review of the Silicon Material Task," JPL Publication 84-24, February 1, 1984.
4. "Proceedings of the Flat-Plate Solar Array Workshop on the Science of Silicon Material Preparation," JPL Publication 83-13, Jet Propulsion Laboratory, Pasadena, California, February 1, 1983.
5. "Feasibility of the Silane Process for Producing Semiconductor- Grade Silicon," Final Report Phases I and II, DOE/JPL 954334- 79/10, Union Carbide Corporation, Washougal, Washington, June 1979.
6. "Experimental Process Development Unit for Producing Semiconductor-Grade Silicon Using the Silane-to-Silicon Process," Final Report, Phase III, DOE/JPL 954334-21, Union Carbide Corporation, Washougal, Washington, 1983.
7. Mui, Y.P., "Investigation of the Hydrogenation of  $\text{SiCl}_4$ ," Final Report, DOE/JPL 955382-79/8, Massachusetts Institute of Technology, Cambridge, Massachusetts, April 1981.
8. Mui, Y.P., "Investigation of the Hydrogenation of  $\text{SiCl}_4$ ," Final Report, DOE/JPL 956061, Solarelectronics, Inc., Bellingham, Massachusetts, 1982.
9. Kim, K., et al., "Modeling of Fluidized-Bed Silicon Deposition Process," JPL Publication 77-38, Jet Propulsion Laboratory, Pasadena, California, June 1977.
10. Praturi, A., et al., "Modeling of Silicon Particle Growth," JPL Document 5101-105, Jet Propulsion Laboratory, Pasadena, California, April 15, 1979.
11. Hogle, R., et al., "In-House Study: Fluidized-Bed Silane Pyrolysis," JPL Document 5101-89, Jet Propulsion Laboratory, Pasadena, California, December 1, 1978.
12. Rohatgi, N.K., et al., "Silane Pyrolysis in a Fluidized-Bed Reactor," Proceedings of the 3rd Symposium on Material of New Processing Technologies for Photovoltaics, J. Electrochem. Soc., Vol. 82-8, pp. 477-487, 1982.

13. Rohatgi, N., and Hsu, G., "Silicon Production in a Fluidized-Bed Reactor: A Parameter Study," JPL D-1283, Jet Propulsion Laboratory, Pasadena, California, October 1983.
14. Levenspiel, O., "The Chemical Reactor Omnibook," Oregon State University Bookstore, Inc., Corvallis, Oregon, 1979.
15. Peters, M.H., Fan, L.S., and Sweeney, T.L., AIChE J, Vol. 28, No. 1, 39, 1982.
16. Tardos, G., Gutfinger, C., and Abuaf, N., Isr. J. Technol. Vol 12, 184, 1974.
17. Hsu, G., Hogle, R., Rohatgi, N., and Morrison, A., J. Electrochem. Soc., Vol. 131, No. 3, p. 660, March 1984.
18. Baker, R.T.K., J. Catal., Vol. 78, 473, 1982.
19. Bokros, J.C., chapter entitled "Deposition, Structure and Properties of Pyrolytic Carbon," in Vol. 5, Chemistry and Physics of Carbon: P.L. Walker, Jr. (Ed.), Marcel Dekker Inc., New York, 1969.
20. Kaae, J.L., Gulden, T.D., and Liang, S., Carbon, Vol. 10, p. 701, 1972.
21. Hogness, T., Wilson, T.L., and Johnson, W.C., J. Am. Chem. Soc., Vol. 58, 108, 1936.
22. Iya, S., Flagella, R.N., and dePaolo, F., J. Electrochem. Soc., 129. No. 7, p. 1531, 1982.



## APPENDIX

### TECHNOLOGY TRANSFER

The JPL in-house technology developed for the fluidized-bed silicon-deposition process was transferred to the interested technical community outside of JPL by making informed presentations to visitors, presenting papers at technical meetings, and publishing reports and papers in technical journals. A brief summary of these activities is outlined as follows:

#### A. VISITOR AND VISITS

##### 1985

Three Japanese scientists, S. Shigeta of the New Energy Development Organization, K. Kaneko of Shin-Etsu Chemical Co., Ltd., and T. Saitoh of Hitachi, attended the 25th Project Integration Meeting (PIM) and held discussions with Project personnel on the direction of the Japanese and American crystalline-silicon solar energy programs.

On February 21, R.G. Boykin and Pete Browning of the Great Lakes Chemical Corp. visited JPL's in-house fluidized-bed reactor lab and discussed its current status with George Hsu (JPL). They indicated that Great Lakes Chemical is actively investigating its expansion into the silicon business.

T. Noda, T. Shirai, and M. Tshi of Osaka Titanium Corp. (OTC), of Amagasaki Hyogo, Japan, visited R. Lutwack, et al., on February 13 to discuss Japanese technology for polysilicon production.

##### 1984

On August 27, JPL was visited by Dr. J. Brian Clark, Chief Director of the Council for Scientific and Industrial Research, National Institute for Materials Research, Pretoria, South Africa. The purpose of his visit was to discuss the status of silicon-refinement technology development within the FSA project and in general. During his visit, Clark met with A.D. Morrison and R. Lutwack, FSA Advanced Materials Research Task.

Professors S. Morimoto and Dr. Y. Shimizu, both of Tokushima University, Japan, visited JPL on August 21. Professor Morimoto described catalyst research for chlorosilane redistribution, and Dr. Shimizu discussed fluidized-bed reactor technology.

Toshio Noda, Osaka Titanium Co. (OTC), Japan, visited JPL on May 24 to discuss the technology for the preparation of polycrystalline silicon with personnel of the FSA Project and the Photovoltaic Program Analysis and Integration (PA&I) Center. Investigations being conducted both in Japan and at JPL for developing fluidized-bed technology were described. Trichlorosilane is the precursor used in the OTC process. Their technical problems deal with wall deposits, seed preparation, and impurities. OTC also is developing a casting procedure under the New Energy Development Organization (NEDO) program. The 1984 goal of the program is the demonstration of technology for the production of 10% efficient cells. In 1985, the goal will be raised to 12% efficient cells.

Toshio Shraiwa and Michi Ishiguro of the Osaka Titanium Co. (OTC), Japan, visited the JPL facilities.

T. Fitzgerald, Rossmore, California, a consultant to JPL, and J. Routbort, Argonne National Laboratory, Argonne, Illinois, visited the JPL laboratories.

Four visitors from Union Carbide Corp., Washougal, Washington, were J. Young, Director of Marketing, Polysilicon Dept., J. Morihara, Manager of Technology, Electronics Division, S. Iya, Program Manager for the JPL contract for FBR research, and J. Lorenz, a consultant to UCC from Scottsdale, Arizona.

On November 7, J. Truitt and A. Carter of Texas Instruments met with FSA personnel to discuss FBR technology for the silane and trichlorosilane systems. Reactor designs, operating conditions, problems, and successes of these two systems were discussed. Texas Instruments is supporting in-house research on the trichlorosilane FBR process.

T. Knuuttila, Director of Kemira of Finland, and E. Kariola, Attache of the Consulate General of Finland in Los Angeles, met with Project personnel on November 8 for a general discussion of polysilicon technology and market projections. One of the main topics was silicon production involving the use of fluosilicic acid as the raw material.

## 1983

Three staff members from the Cabot Corp., Tuscola, Illinois, met with A. Briglio, R. Lutwack, and G. Hsu, FSA Advanced Materials Research Task, on January 20 and 21. The representatives from Cabot were W. Roemelt, Silicone Industry Manager, K.L. Yang, Plant Manager of Cab-O-Sil Division, and D. Wright, Cab-O-Sil Division Engineer. New silicon production processes were discussed, and they were given a tour of the FSA silicon-FBR facility.

Four representatives of Ametek, Paoli, Pennsylvania, visited the FSA facilities and laboratories on January 14. Discussions were held with numerous FSA personnel during the tour. The representatives were B. Russell, President of Technology, P. Meyer, Manager of Photovoltaic Research, and A. D'Ambrosio.

On February 17, at the request of DOE and the State Department, members of the FSA Project briefed four visitors from Spain on the current state of the art of photovoltaics and projections of expected advancement in the next decade. The visitors included Dr. Dominguez of the Spanish Embassy in Washington, D.C., Drs. Tanarro and Ortin, Ministry of Industry and Energy, and Dr. Oistrach of the National Institute of Industry.

A discussion of the silicon-refinement processes that use FBR technology was held on May 20 with representatives of OTC, Japan. OTC is using trichlorosilane in a quartz FBR and is experiencing problems with silicon deposition on the walls. In both the FSA-DOE-sponsored efforts at JPL and UCC, silane is used in metal-wall reactors. Under the proper operating conditions, silicon deposition on the walls has not been a problem. The visitors toured JPL's FBR research facility, where the silane pyrolysis work is being conducted as part of the FSA Silicon Materials Thrust. Participants in the discussions were Toshio Noda, OTC's chief operating officer, Michi Ishiguro, OTC's international affairs manager, and R. Lutwack, G. Hsu, and N. Rohatgi of the FSA Advanced Materials Research Task.

On March 31, F. Yager of the Fraunhofer Institute for Systems and Innovation (ISI) Research, Karlsruhe, and A. Rauber of the Fraunhofer Institute for Solar Energy Systems (ISE), Freiburg, Federal Republic of Germany, visited the following JPL personnel: W. Callaghan, Manager of the FSA Project; P. Henry, Manager of the PA&I Area; and R. Lutwack, Advanced Materials Research Task. They discussed prospects for photovoltaic applications in the United States and Europe. During the year, ISI and ISE will be working on an assessment of the future of photovoltaic solar-energy conversion, including a review of the various photovoltaic development efforts, and the technical and economic aspects of Governmental support measures. The visitors toured the laboratory where JPL's FSA-supported in-house work on pyrolysis of silane in FBRs is being conducted.

S. Timsit, of Alcan Research Laboratory, Kingston, Ontario, Canada, visited R. Lutwack, Advanced Materials Research Task, on April 13 for an exchange of information on the technology of crystal growth and the physics of surfaces. Alcan is in the planning stage of setting up a laboratory devoted to solar cell research, which Dr. Timsit will direct. K. Dumas, T. Daud, and D. Burger, Photovoltaic Components Research Area, led a tour of JPL laboratories for solar cell fabrication and material characterization.

Stephen Lord, J.C. Schumacher Company, Oceanside, California, visited R. Lutwack and G. Hsu, Advanced Materials Research Task, on April 15 to discuss silicon refinement using FBR technology. Schumacher is a producer of dopant chemicals for the semiconductor industry and has been developing a bromosilane process for polysilicon production. FBRs have been his first choice for both the bromosilane formation and silicon deposition steps. Lord toured the JPL laboratory where FSA-supported work on silane pyrolysis in FBRs is being conducted.

#### 1982

J. Bezuidenhoudt and A. Hobkirk of the South African Industrial Development Corp., accompanied by G.H. Schwuttke of IBM, visited JPL on May 3 to discuss the two silicon-production processes (Hemlock's dischlorosilane process, and UCC's silane-to-silicon process) that are under development as part of the FSA Silicon Material Task.

On May 29, three representatives of OTC, Japan, T. Noda, Chief Operating Officer and First Executive Vice-President, M. Ishiguro, Overseas Manager, and T. Shirai, Manager of Patent and Technical License, met with R. Lutwack, A. Briglio, and G. Hsu, of the FSA Silicon Material Task, and discussed silicon-production processes.

A miniworkshop on "Science of Silicon Material Preparation" was held on December 9 and 10 at San Diego State University, California, to discuss the structure of a research program on the phenomena of silane decomposition. The workshop was chaired by R. Lutwack, FSA Advanced Materials Research Task. A series of experiments was proposed to identify the chemical path by which silicon is deposited from silane, and to identify the conditions under which fines are formed and collected in FBRs. Possible methods for preparing reactor seed particles were also proposed.

#### 1981

No reported visits or visitors.

#### 1980

Representatives of Allied Chemical Corporation met with members of the Low-Cost Silicon Solar Array (LSA) Project's Silicon Material Task to discuss polysilicon process technology.

#### Prior to 1980

Visits or visitors were not documented.

## B. TECHNICAL MEETINGS

A paper titled "Chemical Vapor Deposition of Silicon from Silane Pyrolysis," by A.K. Praturi was presented at the Sixth International Conference on Chemical Vapor Deposition, Atlanta, Georgia, October, 1977.

A paper titled, "Silane Pyrolysis in a Fluidized-Bed Reactor," by N. Rohatgi, G. Hsu, and R. Lutwack was presented at the meeting of the Electrochemical Society, Montreal, Canada, May 10-14, 1982.

"Fluidized-Bed Silicon Deposition," by G. Hsu, A. Morrison, N. Rohatgi, R. Lutwack, and T. MacConnell, was presented at a poster session at the 17th IEEE Photovoltaic Specialists Conference, Orlando, Florida, May 1-4, 1984.

A paper titled "Silicon Particle Growth in a Fluidized-Bed Reactor," written by G. Hsu, N. Rohatgi, and J. Houseman, was presented at the AIChE Annual Meeting, San Francisco, California, held November 25-30, 1984. The paper described models for silicon particle growth and their good correlation with experimental data.

Progress reports were presented at every DOE FSA-PIM. These reports are available from Solar Data Center, Jet Propulsion Laboratory, Pasadena, California.

W. Callaghan and R. Lutwack attended the Sixth European Photovoltaic Solar Energy Conference on April 15-19, 1985, in London, England. W. Callaghan participated in a panel discussion on "Material Problems of the PV Industry," and presented a paper titled "Flat-Plate Solar Array Project: Progress and Plans." R. Lutwack cochaired a session on crystalline silicon and presented a paper titled "New Polycrystalline Silicon Refining Technology and the Silicon Supply Outlook for the Photovoltaics Industry."

## C. PUBLISHED REPORTS AND TECHNICAL PAPERS

"Modeling of Fluidized-Bed Silicon-Deposition Process," by K. Kim, G. Hsu, R. Lutwack, and A. Praturi, JPL Publication 77-38, Jet Propulsion Laboratory, Pasadena, California, June 15, 1977.

"Modeling of Silicon Particle Growth," by A. Praturi, G. Hsu, and R. Lutwack, JPL Document 5101-105, Jet Propulsion Laboratory, Pasadena, California, April 15, 1979.

"Chemical Vapor Deposition of Silicon from Silane Pyrolysis," by A. Praturi, Proceedings of the Sixth International Chemical Vapor Deposition Conference, L.F. Donaghey, P. Raichoudhery, and R.N. Tanber, (Eds.), pp. 2024, The Electrochemical Society, Inc., Princeton, New Jersey, 1977.

"In-House Study: Fluidized-Bed Silane Pyrolysis," by R. Hogle, G. Hsu, and R. Lutwack, JPL Document, 5101-89, Jet Propulsion Laboratory, Pasadena, California, December 1, 1978.

A paper titled "Silane Pyrolysis in a Fluidized-Bed Reactor," written by N. Rohatgi, G. Hsu, and L. Lutwack, FSA Advanced Materials Research Task, was published in the Proceedings of the Third Symposium on Materials and New Processing Technologies for Photovoltaics, Vol. 82-8, p. 477-487, 1982. This symposium was held in connection with the 161st Electrochemical Society Meeting at Montreal, Canada, May 10-14, 1982.

JPL Publication 83-13, dated February 1, 1983, titled "Proceedings of the Flat-Plate Solar Array Workshop on the Science of Silicon Materials Preparation," documented the workshop held August 23-25, 1982. The report was edited by R. Lutwack, Advanced Materials Research Task, and is part of the Silicon Materials Thrust.

"Silicon Production in a Fluidized-Bed Reactor: A Parameter Study," by N. Rohatgi and G. Hsu, JPL D-1283, Jet Propulsion Laboratory, Pasadena, California, October 1983.

A Review of the Silicon Material Task," R. Lutwack, JPL Publication 84-24, Jet Propulsion Laboratory, Pasadena, California, February 1, 1984.

"Fines in Fluidized-Bed Silane Pyrolysis," by G. Hsu, R. Hogle, N. Rohatgi, and A. Morrison, published in the Journal of the Electrochemical Society, Vol. 131, No. 3, March 1984.

"Fluidized-Bed Silicon Deposition," by G. Hsu, A. Morrison, N. Rohatgi, R. Lutwack, and T. MacConnell, published in the Proceedings of the Seventh IEEE Photovoltaic Specialists Conference, pp. 553-557, May 1-4, 1984.